FINAL REPORT
PROJECT NO. A-413

PORCELAIN ENAMELING QUALITY STEEL PLATES

By

J. N. HARRIS and J. D. WALTON

****

Contract No. NObs 77022
Index No. NS-061-200
Bureau of Ships Code 312
Department of the Navy

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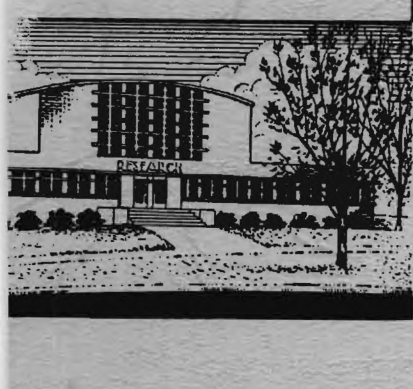
GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

January 31, 1960



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

4-4-60

CODE SHEET

The following code designates manufacturers of materials listed in this report.

Code	Manufacturer
H	Youngstown Sheet and Tube
J	Jones and Laughlin Steel
L	Lukens Steel
N	Alan Wood Steel
T	Bethlehem Steel
W	United States Steel
+1-b	O. Hommel Clay No. 540
1-d	O. Hommel Clay No. 528
++1-e	O. Hommel Clay No. 540
1-f	O. Hommel Clay No. 842
1-g	O. Hommel Clay No. 999
2	Ferro Green Label Clay
3	Ferro Red Label Clay
4	Ferro Black Label Clay

\+ obtained from O. Hommel

++ obtained from the Warren Company, Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
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I. SUMMARY

A recommended procedure for qualification of steel plate was developed. This method includes coating of steel plate with a standard enamel and subjecting the coated plates to gas extraction, accelerated fishscale and thermal spalling tests. Those plates which after enameling exhibit low extractable gas (less than 0.30 ml for 3/16 inch specimens) negative accelerated fishscale and no spalling can be considered qualified.

Work was carried out to develop a standard slip to be used as a qualifying test for discriminating between enameling and non-enameling quality steel plate. This work included a study of the possibility of laboratory smelting of reagent frits for use in a standard qualifying slip. This was abandoned in favor of purchasing large quantities of commercial frit all from the same batch since it would be most difficult to duplicate smelting results in the laboratories of each agency that might have cause to smelt these frits. The purchasing and storing of large quantities of commercial frits would appear to offer assurance of a constant product for use as a reagent material.

An effort was made to develop specifications for a standard clay for use in a standard slip using differential thermal analysis and visual observations of the bubble strata of a porcelain enameled plate prepared with the clay being studied. These criteria appear to be satisfactory for selecting a standard clay.

A brief study was made of a method for eliminating clay as a variable in the gas extraction study by immersing metal samples in fused silica crucibles containing molten frit only, and crucibles containing molten frit and clay mixtures. This test was not considered practical due to the large

amounts of gas extracted from the samples, the large quantities of materials required and the long processing time required.

Liquid nitrogen was studied as a possible quenching medium for gas extraction specimens. However, the relatively slow cooling rate of metal specimens quenched in liquid nitrogen as compared with the cooling rate in water eliminated its use. Water, therefore, continued to be used as the quenching medium for gas extraction specimens.

Fused alumina was added to the standard qualifying mill batch and a study of its effect on gas extraction was carried out. No definite relationship between gas extracted and tendency to fishscale was shown, nor did the values show any relationship to those obtained from the alumina free enamel.

Gas extracted from specimens coated with both the standard qualifying enamel and with the alumina bearing standard qualifying enamel increased with carbon content up to 0.12 carbon. Above this carbon content the average amount of gas extracted remained essentially constant, although wide variations in extractable gas from individual samples was noted. The fused alumina caused a reduction in the variation of the amount of gas extracted.

Qualification studies on eight 3/16-inch steels and four 1/4-inch steels were carried out using the standard enamel. All but one of the 3/16-inch plates (J-1) and all but one of the 1/4-inch plates (W-2) passed the requirements of MIL-P-16961B.

The reason for failure of the enamel coatings on specimens J-1 and W-2 was not apparent from the chemical composition, heat history, or the gas extraction studies. Photomicrographs of the enamel metal interface of each steel were prepared in an effort to determine cause of failure of the enamel on these two specimens. No unusual variation was noted in any of the photomicrographs which might have been responsible for failure of the enamel coating on the two steels in question.

Eight T-joint specimens and twelve 4- by 8-inch steel plates were coated commercially. Six of the steel plates and two of the T-joints did not meet the thermal quench requirement. The commercial coating was also applied at Georgia Tech to 4- by 8-inch plates of each of the twelve steels. This coating was fired at Georgia Tech in the same "wet" atmosphere used with the standard qualifying enamel. Upon cooling, the coating fishscaled on nine of the twelve steels tested.

II. INTRODUCTION

The principal objective of this work was to develop a complete and technically accurate description of steel plate and weldments of steel plate acceptably receptive to porcelain enamel coatings; said description being suitable as an aggregate of technical requirements, for being incorporated into material specifications for Government procurement.

This contract was the third in a series covering studies on the enameling quality of steel plate and welds. At the conclusion of the second contract a possibility was indicated that this attribute of steel plate might be assessed by test enameling with "reagent" materials (frit and clay), observing spalling and fishscaling tendencies and measuring the extractable gas content of the coated sample. Therefore, the work reported herein covers a program of experiments, results of which throw light on the problems involved and the apparent impracticability of setting a standard "reagent" frit in laboratory batch quantities.

From the results of the first two years work a number of test procedures were developed which might possibly be incorporated in a specification for enameling quality steel plates. Among those which appeared to be most promising were: (1) gas extracted from a steel specimen coated with a standard enamel which was quenched immediately upon removal from the furnace, (2) accelerated aging of enameled specimens to cause fishscaling defects to appear by heating enameled specimens to an elevated temperature for 24 to 48 hours and (3) thermal quenching of enameled specimens by immersion, or by a water-jet on one surface of the specimen.

From the results of the first two years work a possible procedure was set up for qualifying steel plate acceptably receptive to porcelain enamel coatings by the use of a "standard qualifying enamel." This report describes the work carried out in developing a "standard qualifying enamel" and the qualification of steel plate intended for porcelain enameling.

During the first two years, experiments were carried out whereby the gas diffusion properties of steel could be determined as well as the amount of gas injected into a steel sample during enameling. The latter test depending on the amount of gas being extracted from the steel after enameling. Gas extraction data showed that increased firing time, steel thickness and moisture in the furnace atmosphere all increased the amount of gas extracted. No correlation appeared evident between the carbon content or (tendency to fishscale) of different steels and the amount of gas extracted.

Four new low temperature ground coat enamels and various grades of steel in 3/16 and 5/8 inch thickness were obtained for study. Studies were made with these materials to determine the effects of type of enameling clay used, mill additions, firing atmosphere, firing temperature and length of firing time.

In order to better evaluate weldments, welding electrodes were studied from the standpoint of affinity for moisture of the electrode coating. The defects produced on porcelain enameled welds were also studied using a variety of electrodes by AWS classification and using a series of welding techniques designed to produce welds that cause defects.

III. EXPERIMENTAL WORK

A. Standard Qualifying Enamel Slip

1. Standard Qualifying Frit

Work under the previous contract has shown that commercial porcelain enamel frits may vary from batch to batch. If a porcelain enamel slip is to be used to determine the suitability of steel plate to be enameled either a large quantity of commercial frit all smelted from the same batch must be kept on hand or a "reagent" or "standard-qualifying" frit must be prepared under strictly supervised laboratory conditions so that variables in the frit are reduced to a minimum.

a. Technology of Smelt Batch Formulation

The composition and physical properties of porcelain enamel vary widely from those of conventional glasses. The formulation of glasses for porcelain enamels must be so adjusted as to maintain certain physical properties within specified ranges. Properties which must be considered are: thermal expansion, temperature and time required to mature the coating, water solubility, compatibility with the metal, adherence of the glass to iron and retention of glass properties after repeatedly being heated to temperatures above the softening point. Although silica is the major component of all glasses, it has some undesirable properties as related to its use in porcelain enamels. The melting point of silica is too high and the expansion is too low for use alone as an enamel on steel; therefore, other components must be added to give the glass phase the properties desired. To lower the melting point of the glass, fluxes such as sodium oxide, potassium oxide, calcium oxide, lithium oxide and boron oxide are commonly used. Expansion of the glass is sometimes controlled by variations in the amount of boron oxide and sodium oxide added to the smelt batch, since boron oxide has a relatively low coefficient and sodium oxide a high coefficient of thermal expansion. Fluorine is also sometimes used as a fluxing agent added as Fluospar (CaF_2). In this way calcium oxide and fluorine can be added to the smelt batch in one material. The adherence of the glass to iron can be promoted by the addition of manganese oxide, cobaltous oxide, and nickel oxide. Small additions of aluminum oxide are added to improve the durability of glasses.

Smelting involves the melting together of the raw materials in the composition until a uniform glass is formed. The success of this operation is dependent on the thorough mixing of the raw materials, the proper heating and the distribution of the heat through the batch. Some materials in the batch are volatile, some fuse readily, some decompose and some are highly refractory. The readily fusible materials melt first giving a sticky mass which impedes the evolution of volatile materials. The volatiles become occluded and absorbed by the melt. The refractory materials are taken into solution. The fundamental changes taking place in the melt are: (1) interaction of acids and bases, (2) decomposition, (3) fusion and (4) solution. In the early stages of smelting, the melting of materials and the steam produced from materials giving up their water of crystallization cause considerable agitation in the batch. Due to decomposition of carbonates in the batch, carbon dioxide is given off up to temperatures of 1750°F providing further agitation.

If the enamel batch is heated too rapidly, the more fusible constituents are melted and volatilized before they can react with the more refractory materials. This results in a final batch, which is more refractory than it would have been if less of the flux had been driven off.

b. Preparation of "Standard Qualifying Frits"

Frits S-1, S-2 and S-3 were thought to be suitable for incorporation into a "standard-qualifying" slip and their compositions were determined by spectrographic and wet chemical analyses. The results of these (in oxide equivalents) appear in Table I.

TABLE I

OXIDE COMPOSITIONS OF STANDARD FRITS

Oxide	Frit Numbers		
	S-1	S-2	S-3
SiO_2	29.70	27.88	30.66
Al_2O_3	6.25	4.02	1.54
B_2O_3	14.77	19.03	19.70
Na_2O	15.68	21.03	11.08
K_2O	1.25	0.29	3.25
Li_2O	0.15	----	0.05
CaO	10.01	10.06	14.01
CaF_2	1.91	0.55	1.91
MnO_2	0.10	0.02	0.11
CoO	0.86	1.22	1.30
NiO	1.53	2.03	0.19
ZnO	1.00	----	----

From these analyses, the batch compositions of S-1A, S-2A and S-3A shown in Table II were calculated.

In order to determine the proper smelting temperature for the new frit batches samples of frits S-1, S-2, and S-3 were melted in a gas fired, crucible furnace to the proper consistency. The time of melting and the temperature of the melted frit were used as guides for smelting the batch compositions S-1A, S-2A and S-3A.

Laboratory quantities of frit were prepared by smelting 1500 gram batches in the furnace. The well mixed batch was charged into a hot crucible and toward the end of the smelting, the batch was stirred with a clean iron rod (Figure 1). Samples were taken from time to time by drawing a fine thread of melted frit from the end of the rod (Figure 2). Smelting was considered complete when the thread was free of unmelted material and it could be drawn into a small loop without breaking. The smelted material was then poured into cold water for fritting (Figure 3).

Due to losses of volatile material in the smelting operation, the theoretical oxide content could not be taken to be the same as the melted composition. The smelted batches were examined spectrographically and compared with the spectrographic analysis of frits S-1, S-2 and S-3 (standards). The spectrographic analysis of frits S-1A, S-2A and S-3A appears in Table III.

Fluorides are violent fluxes and greatly aid the fusibility of the glass during the smelting operation. However, these fluorides may be partially volatilized during the melting of the glass. In order to determine the amount of fluorides lost in the smelting operation the per cent fluorine in each of the smelted frits was measured by wet chemical

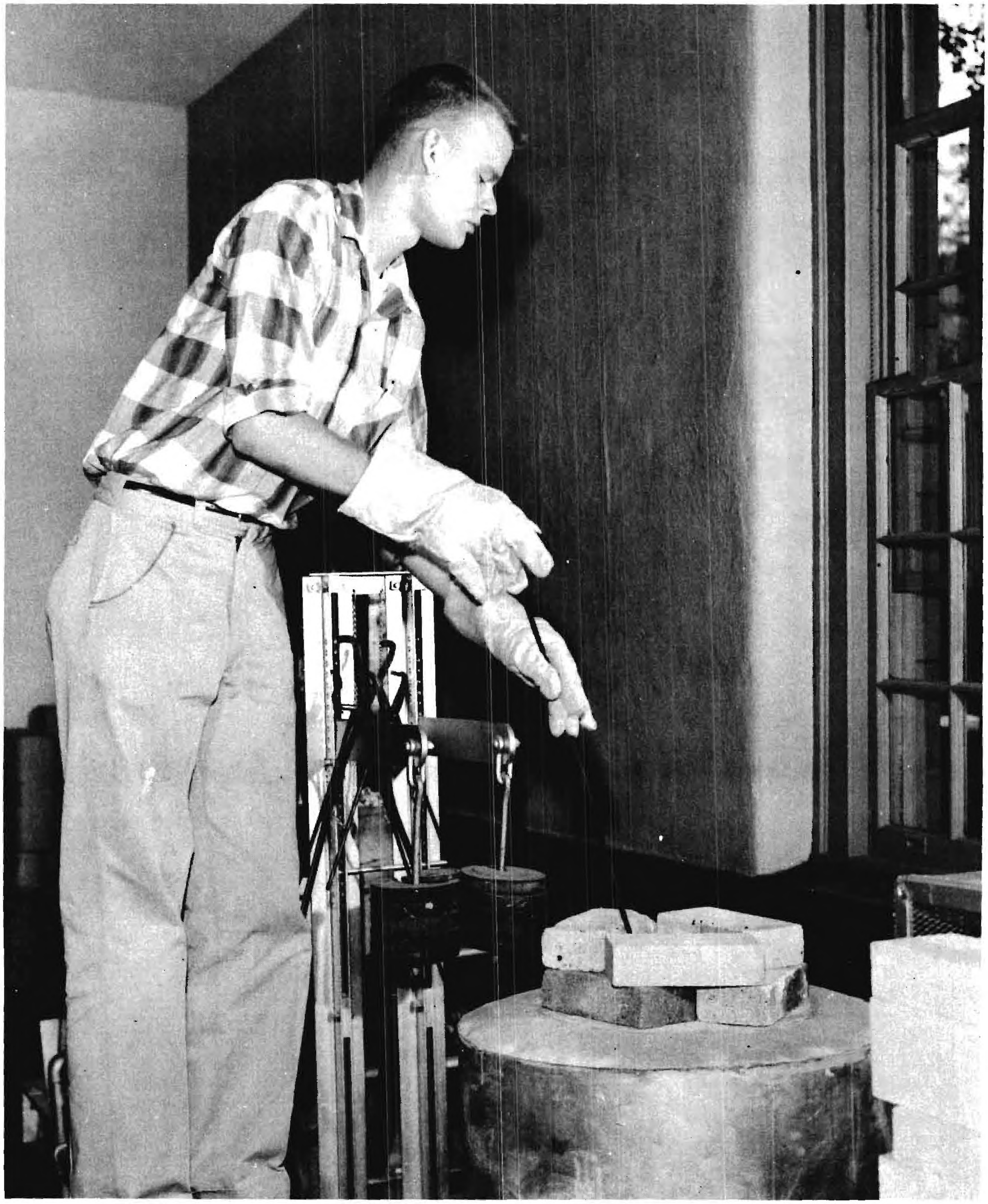


Figure 1. Stirring of the Smelt Batch in the Crucible Furnace.

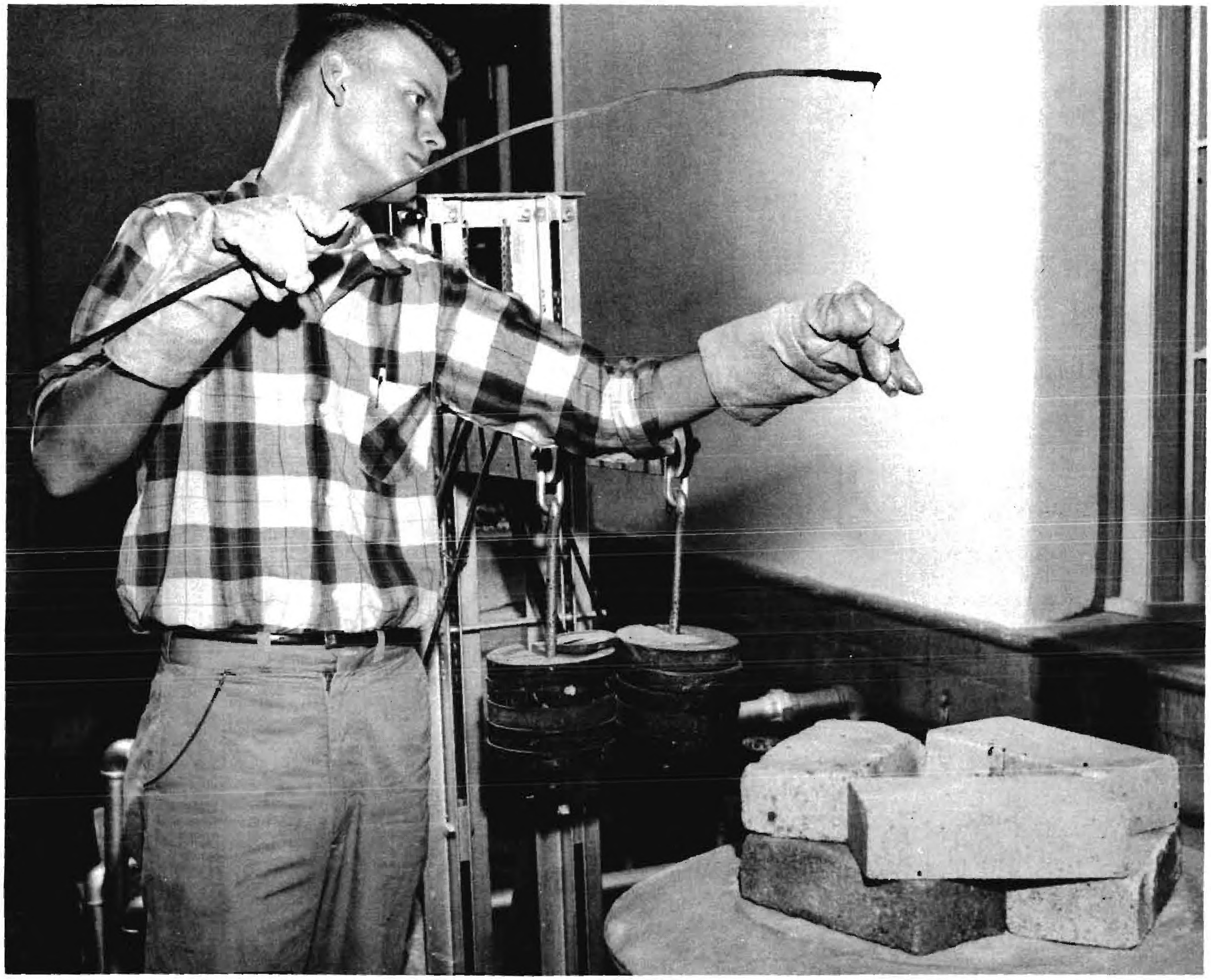


Figure 2. Thread Test for Completeness of Smelting.

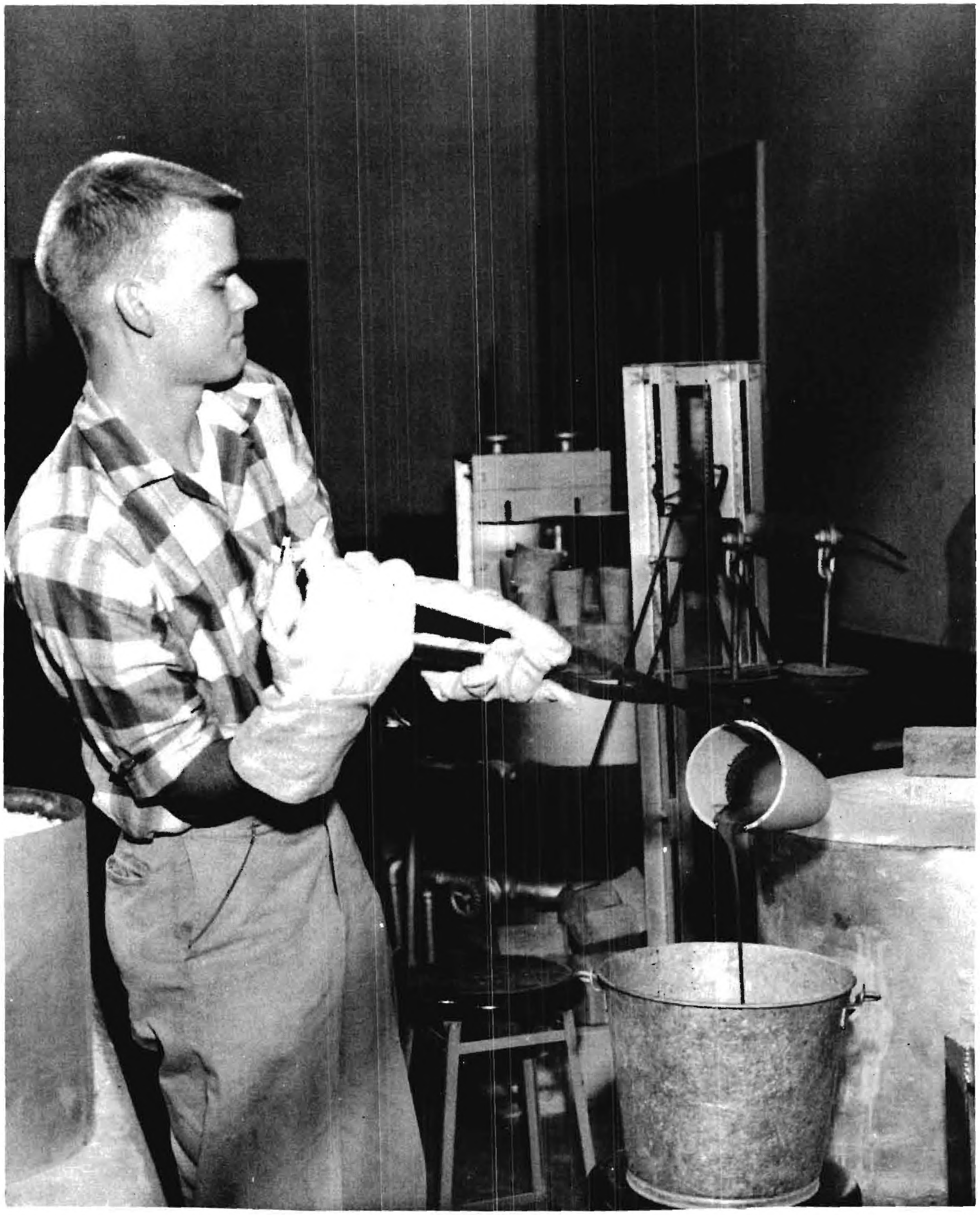


Figure 3. Quenching of the Molten Frit Batch.

analysis.

To determine further the characteristics of the smelted frits in comparison with frits S-1, S-2 and S-3 (standards), fusion flow tests were carried out according to ASTM method C374-55T. Briefly, this method consists of crushing particles of frit in a mortar to pass a 12 mesh screen and to be retained on a 200 mesh screen. Three-and-a-half-gram samples were then weighed and mixed with 4 or 5 drops of water. Fusion buttons were then pressed in a 1/4 inch die under 4000 pounds pressure. The button specimens were dried and placed on a fired ground coat plate, along with a standard fusion button prepared from one of the standard frits (S-1, S-2 or S-3)

TABLE II

BATCH COMPOSITION OF
"LABORATORY STANDARD QUALIFYING FRITS"
(INITIAL SMELT)

Constituents	Frit Numbers		
	S-1A (%)	S-2A (%)	S-3A (%)
SiO_2	21.50	21.15	21.50
$Al(OH)_3$	6.55	4.60	-----
Borax (Hydrous)	34.85	40.53	45.88
K-Feldspar	6.39	0.90	7.17
Li_2CO_3	0.32	----	0.11
Fluorspar	12.04	10.92	16.63
MnO_2	0.09	0.08	0.09
Co_3O_4	0.80	1.02	1.19

TABLE II (Cont.)

BATCH COMPOSITION OF
"LABORATORY STANDARD QUALIFYING FRITS"
(INITIAL SMELT)

Constituents	Frit Numbers		
	S-1A (%)	S-2A (%)	S-3A (%)
NiO	1.32	1.58	0.16
KNO_2	----	----	3.35
Na_2CO_3	10.54	12.80	2.71
$NaNO_2$	4.73	6.41	1.17
ZnO	0.86	----	----

The ground coat plate with fusion buttons thereon was placed in a horizontal position on the pre-heated fusion flow rack (Figure 4a) and placed in a furnace at 1300°F until such time as fusion was evident from the rounded appearance of the top of the buttons. The plate was then released to the vertical position and the "fused" buttons allowed to flow at least 5 centimeters (Figure 4b). The plate was then removed from the furnace. The length of the flow of the button being tested was then compared with the standard button.

Fusion flow test buttons made from frits S-1A, S-2A and S-3A were compared with fusion flow buttons made from frits S-1, S-2 and S-3. At 1300°F the buttons made from frits S-1, S-2 and S-3 flowed off the ground coated plate while the buttons made from S-1A, S-2A and S-3A did not flow at all.

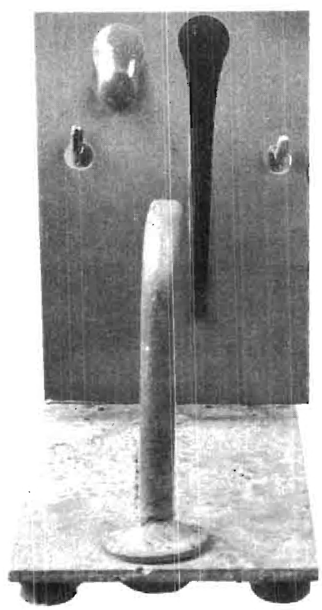
Variations were made in the smelt batch formulations of each of the frits in an effort to duplicate the melted composition of the standard frits. Four additional smelt batch compositions were smelted for each frit. These appear in Table IV through VI. Smelt batches three and five were identical.

TABLE III

MELTED COMPOSITION OF
"LABORATORY STANDARD QUALIFYING FRITS"
(INITIAL SMELT)

Oxide	Frit Numbers		
	S-1A (Wt.%)	S-2A (Wt.%)	S-3A (Wt.%)
SiO_2	38.00	31.00	34.60
Al_2O_3	4.38	4.23	1.42
B_2O_3	17.30	22.80	26.14
Na_2O	19.41	25.20	14.22
K_2O	1.94	0.24	4.31
Li_2O	0.17	----	----
CaO	12.08	12.00	16.20
MnO_2	0.15	0.12	0.37
CoO	1.02	1.70	1.76
NiO	1.83	2.56	0.27
ZnO	3.36	-----	-----

(a) FUSION FLOW BUTTONS IN HORIZONTAL POSITION



(b) FUSION FLOW PLATE IN VERTICAL POSITION

Figure 4. Fusion Test Assembly.

TABLE IV

BATCH COMPOSITION OF
"LABORATORY STANDARD QUALIFYING FRITS"
(SECOND SMELT)

Material	Frit		
	S-1B (Wt.%)	S-2B (Wt. %)	S-3B (Wt.%)
SiO_2	24.92	24.79	29.75
Borax (Anhydrous)	2.88	5.05	1.89
K-Feldspar	20.38	27.13	32.48
Li_2CO_3	9.35	1.15	-----
Fluorspar	0.34	-----	0.01
MnO_2	0.12	1.02	0.31
Co_3O_4	0.89	1.50	1.62
NiO	1.49	2.11	0.23
ZnO	2.74	-----	-----
$NaNO_2$	6.89	6.89	1.69
Na_2CO_3	14.66	15.89	4.62
KNO_3	-----	-----	7.97

In order to determine the adjustments needed in formulating the smelt batches to duplicate frits S-1, S-2 and S-3 the following work was carried out. The melted compositions of each of the frits smelted were determined spectrographically and plotted on ternary diagrams based on the major oxide components of the frits. Adjustments were then made in the raw materials of the batch composition for the next smelt. Figures 5 through 8 show the percentages of each of the major oxides in each frit smelted. It can be seen that some of the smelted frits approach very closely the oxide equivalent composition of frits S-1, S-2, and S-3.

TABLE V

BATCH COMPOSITION OF
"LABORATORY STANDARD QUALIFYING FRITS"
(THIRD AND FIFTH SMELT)

Constituents	Frit Numbers		
	R-1A	R-2A	R-3A
SiO_2	21.75	25.27	26.27
$Al(OH)_3$	6.38	5.29	-----
Borax	22.01	26.95	30.20
Na_2CO_3	11.51	14.32	2.82
$NaNO_2$	5.05	7.61	1.51
K-Feldspar	12.89	2.83	9.09
CaF_2	16.35	14.21	22.74
Li_2CO_3	0.38	-----	0.13
MnO_2	0.10	0.02	0.12
CO_3O_4	0.95	1.28	1.47
NiO	1.58	1.98	0.20
ZnO	1.03	-----	-----
KNO_3	-----	-----	5.45

TABLE VI

BATCH COMPOSITION OF
"LABORATORY STANDARD QUALIFYING FRITS"
(FOURTH SMELT)

Constituents	Frit Numbers		
	R-1B	R-2B	R-3B
SiO_2	18.70	25.25	17.39
$Al(OH)_3$	6.12	5.18	-----
Borax	21.70	25.90	15.50
Na_2CO_3	10.71	15.10	11.94
$NaNO_3$	5.74	8.37	6.37
K-Feldspar	12.45	2.72	11.12
CaF_2	17.90	14.20	29.11
Li_2CO_3	3.12	-----	0.99
MnO_2	0.10	0.17	0.12
Co_3O_4	0.90	1.25	1.91
NiO	1.50	1.79	0.25
ZnO	1.01	-----	-----

The fluorine content of each frit smelted was determined by wet chemical analysis and is listed in Table VII.

Fusion flow tests using frits S-1, S-2 and S-3 as standards indicated that the "laboratory standard qualifying frits" were too refractory since in most cases the standard ran off the plate before the "laboratory standard qualifying frits" had begun to flow. Since the oxide compositions are relatively close, and the fluorine content of the "laboratory standard qualifying frits" is in most cases greater than S-1, S-2 and S-3, it would seem that the frits should have a lower fusion temperature. However, in most cases frits S-1, S-2 and S-3 had lower fusion points.

The available funds, time and press of other work within the scope of the project precluded further effort to develop a laboratory smelted standard frit as a "reagent" material. However, this brief effort in that direction served to illustrate the problems involved in such a program and perhaps suggest difficulties which might arise in attempting to have different laboratories smelt standard frits for the qualification of steel plate. It was therefore suggested that a commercial source of a large quantity of frit from a single smelt or a blend of that frit from more than one smelt be obtained and stored for use in a qualifying enamel.

TABLE VII

FLUORINE CONTAINED IN "LABORATORY STANDARD QUALIFYING FRITS"

Frit No.	Fluorine (%)	Frit No.	Fluorine (%)
R-1A	3.59	S-2	1.20
R-1B	0.38	S-2A	3.61
R-1C	4.64	S-2B	4.85
S-1	2.03	R-3A	3.55
S-1A	0.15	R-3B	12.96
S-1B	3.57	R-3C	7.47
R-2A	3.31	S-3	1.44
R-2B	4.94	S-3A	4.52
R-2C	4.22	S-3B	3.97

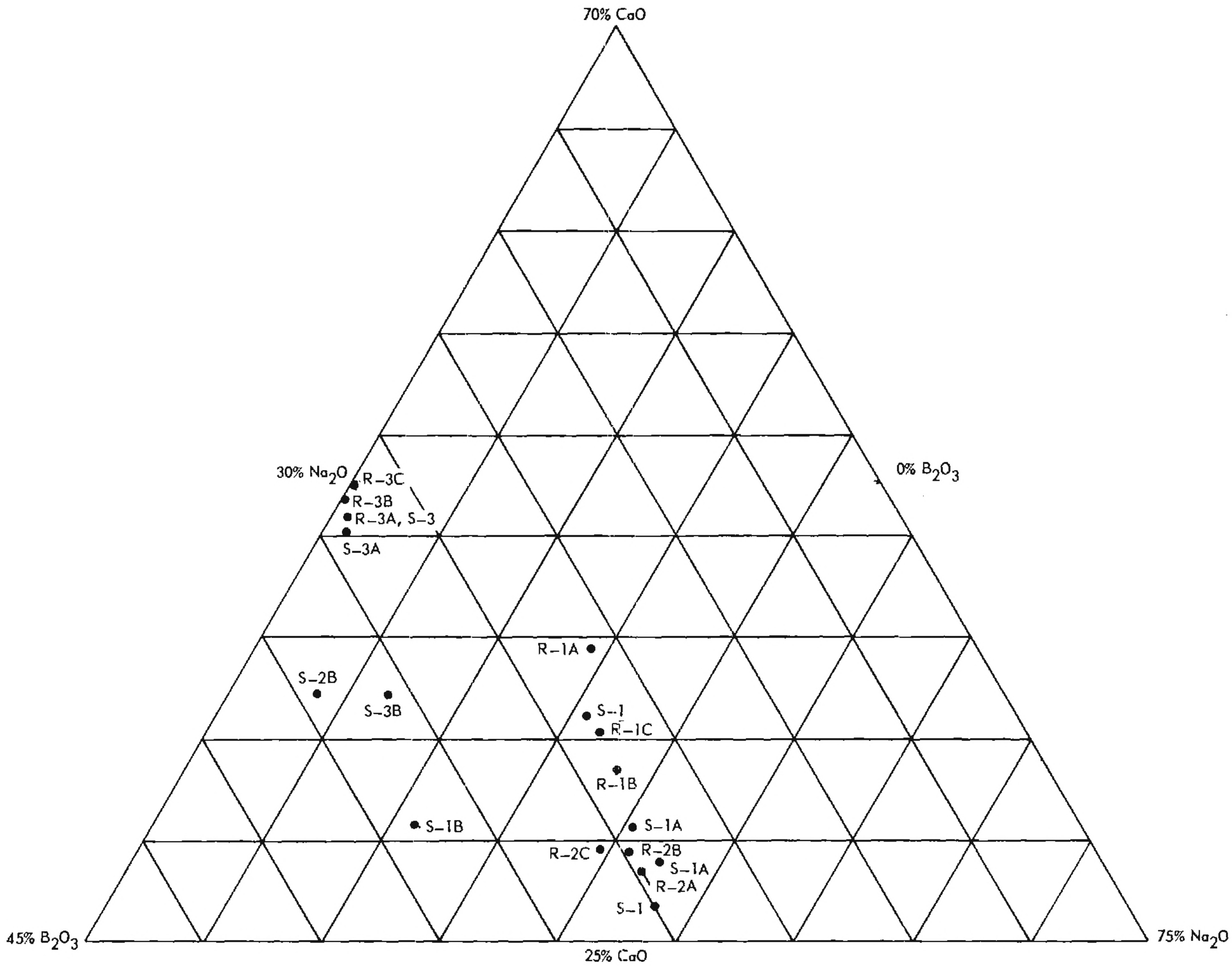


Figure 5. Ternary Diagram of the System B_2O_3, CaO, Na_2O, Showing Chemical Composition of Reagent Frits.

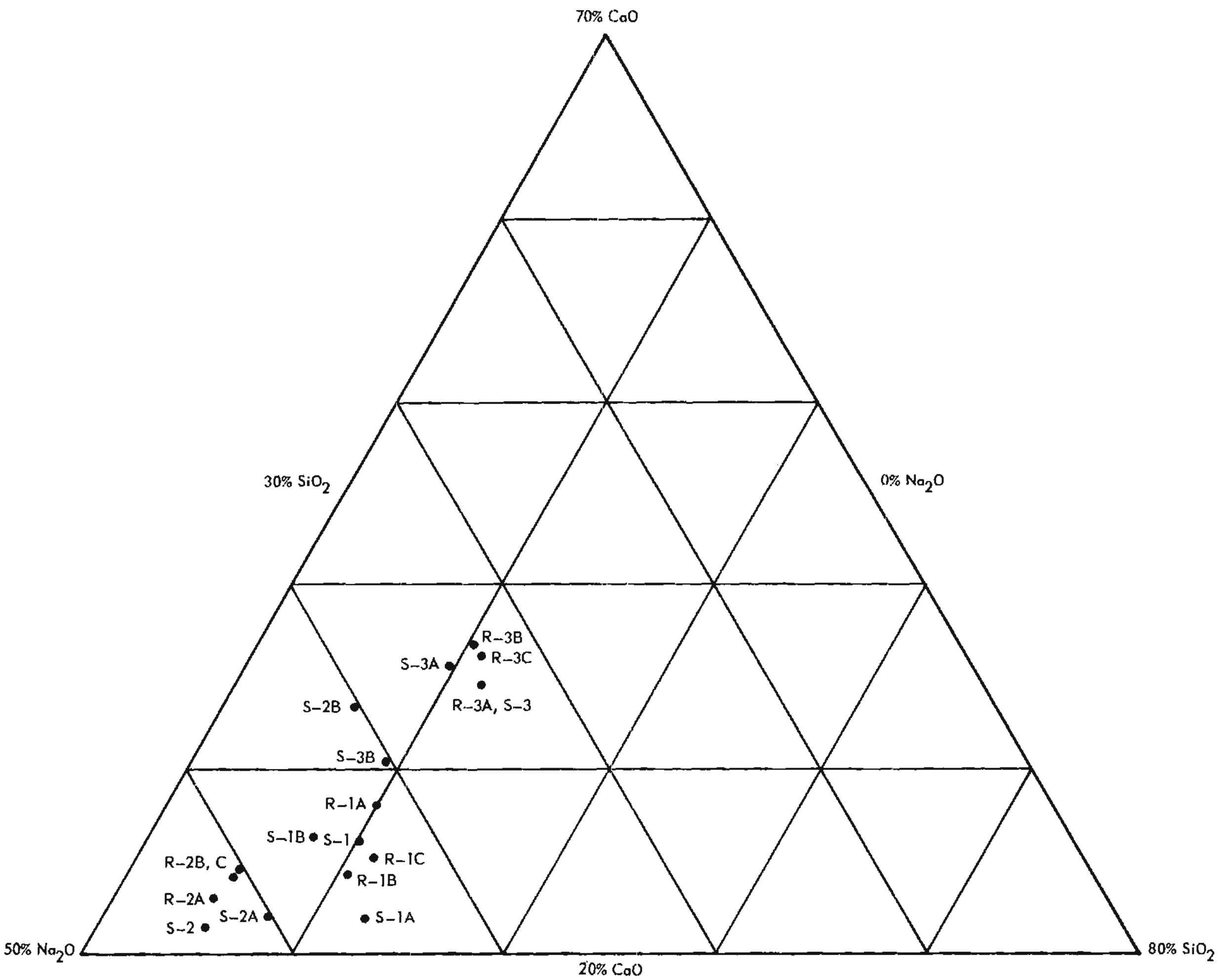


Figure 6. Ternary Diagram of the System Na_2O, CaO, SiO_2, Showing Chemical Composition of Reagent Frits.

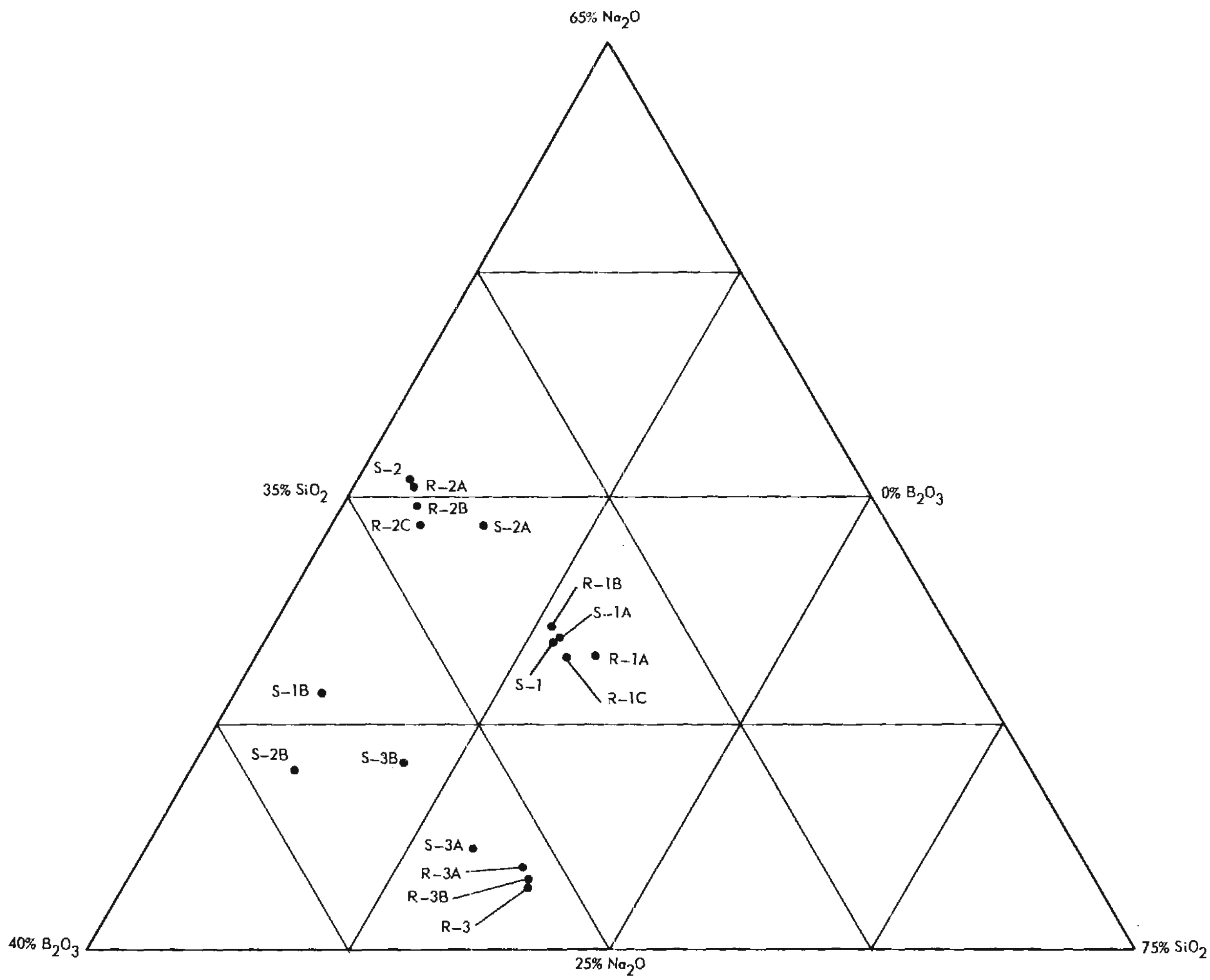


Figure 7. Ternary Diagram of the System B_2O_3, Na_2O, SiO_2, Showing Chemical Composition of Reagent Frits.

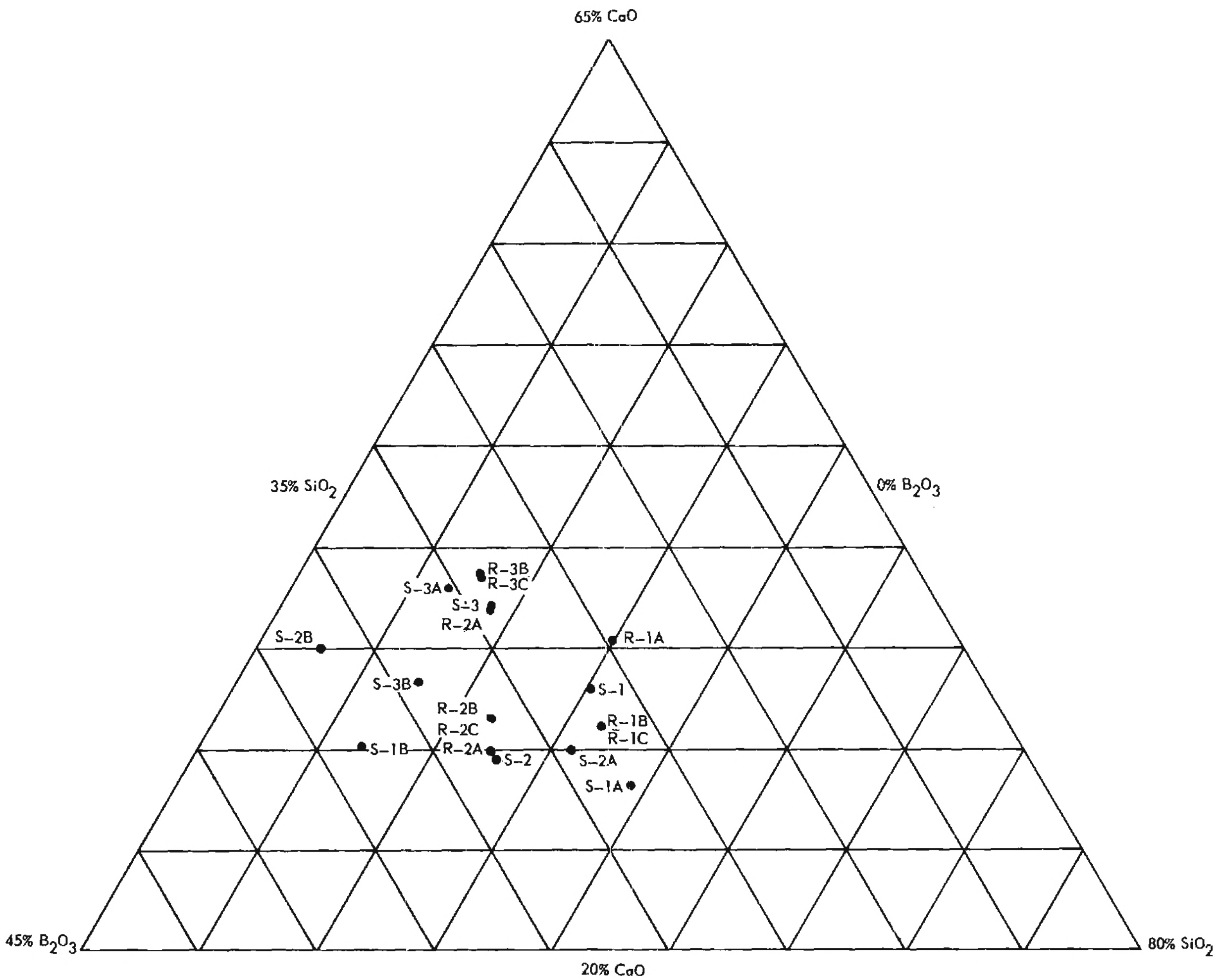


Figure 8. Ternary Diagram of the System B_2O_3, CaO, SiO_2, Showing Chemical Composition of Reagent Frits.

2. Standard-Qualifying Clay

In order to establish standards for a "reagent" clay, eight commercial enameling clays were procured and examined by differential thermal analysis and by the application to steel plate of the standard porcelain enamel containing the clay. The enameled steel plate was observed microscopically to determine the appearance of the bubble stratum.

a. Differential Thermal Analysis

Differential thermal analysis consists of placing two samples of material side by side in an electrical resistance furnace heated at a constant rate to a predetermined temperature. One of the materials being heated is inert, that is, it does not undergo any endothermic or exothermic reactions while being heated. This material is used as a reference. Thermocouples are embedded in both materials and are connected so that any temperature difference between them is recorded as the resultant millivoltage produced by the temperature difference. This produces a differential thermal history curve which is recorded simultaneously with the temperature of the reference material. A plot is then made of the differential temperature as a function of reference temperature.

Differential thermal analysis is used for two purposes: (1) to identify substances and (2) to determine the quantity of reacting material in a sample.

For our purposes differential thermal analysis was used to determine (1) the amount of organic material, (2) the amount of chemical (combined) water and (3) the crystallinity of enameling clays. Of eight enameling clays tested the major differences found were in the amount of chemical water contained and the degree of crystallinity.

In recording the differential millivoltage in the analysis of clays endothermic and exothermic reactions are recorded as peaks. The peak area is that enclosed by the zero-differential line and the peak curve of the differential temperature as recorded versus time. The area under the chemical water evolution portion of the curve can be taken as a relative measure of the amount of chemical water evolved.

The method used for the differential thermal analysis of the enameling clays is essentially the same as that described by Walton.[1] Briefly this method is as follows: Pellets of the clay to be investigated and pellets of calcined clay were prepared by pressing 2.0 grams of each material with a few drops of water as a binder. A force of 750 pounds was used to press the 3/8-inch diameter pellets. A pellet of the clay to be investigated and a pellet of calcined clay were each placed over thermocouples protruding from an inconel block. The samples were then raised into an electrical resistance furnace and heated at a constant rate of $10^{o}C$ per minute to $1000^{o}C$. The thermocouples were connected to a potentiometer twin-pen recorder. One pen recorded the temperature of the reference sample and the other pen recorded the millivolt differential between the two thermocouples. The area defined by the peak drawn by the differential pen for the chemical water evolution portion of the DTA curve and the base line was measured by the use of a planimeter and was taken as a relative measure of the amount of chemical water evolved. This area was measured and reported in square inches as a matter of convenience. The values obtained are recorded in Table VIII. Figure 9 shows two of the original curves. The shaded portion is the area under the chemical water evolution portion of the curve. Figure 10 shows differential thermal

[1] J. D. Walton, Jr. "New Method of Preparing Clay Samples for Differential Thermal Analysis," J. Am. Ceram. Soc. 38, No. 12, 438-443 (1955)

analysis curves for each of the eight clays tested.

TABLE VIII

AREA UNDER CHEMICAL WATER EVOLUTION PORTION
OF DIFFERENTIAL THERMAL ANALYSIS

Clay No.	Sample 1 (in^2)	Sample 2 (in^2)	Average (in^2)
1b	3.6	---	3.6
1d	1.3	1.4	1.35
1e	3.3	3.6	3.45
1f	2.6	2.8	2.70
1g	2.5	2.6	2.55
2	2.9	3.5	3.20
3	3.1	3.2	3.15
4	4.0	4.3	4.15

b. Observation of Bubble Stratum

An effort was made to correlate the results of the differential thermal analysis of each clay with the formation of bubbles in porcelain enamel applied to C1012 steel plate. Each of the eight clays was milled with the mill batch listed below, applied to steel plates and fired.

Standard Mill Batch

65 parts	Frit S-1
15 parts	Frit S-2
20 parts	Frit S-3
6 parts	Clay

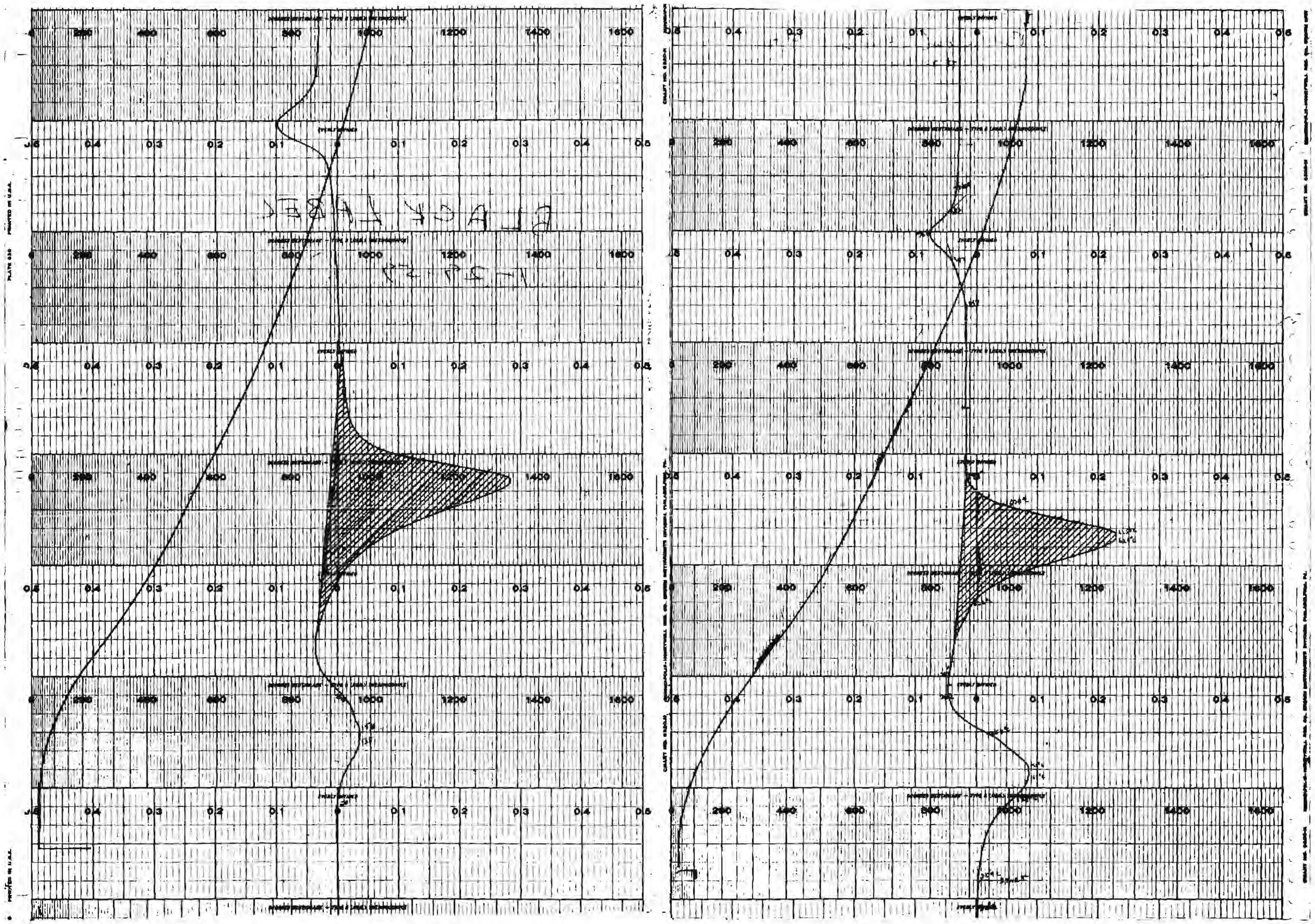


Figure 9. Typical Differential Thermal Analysis Curves Drawn by Twin Pin Recorder.

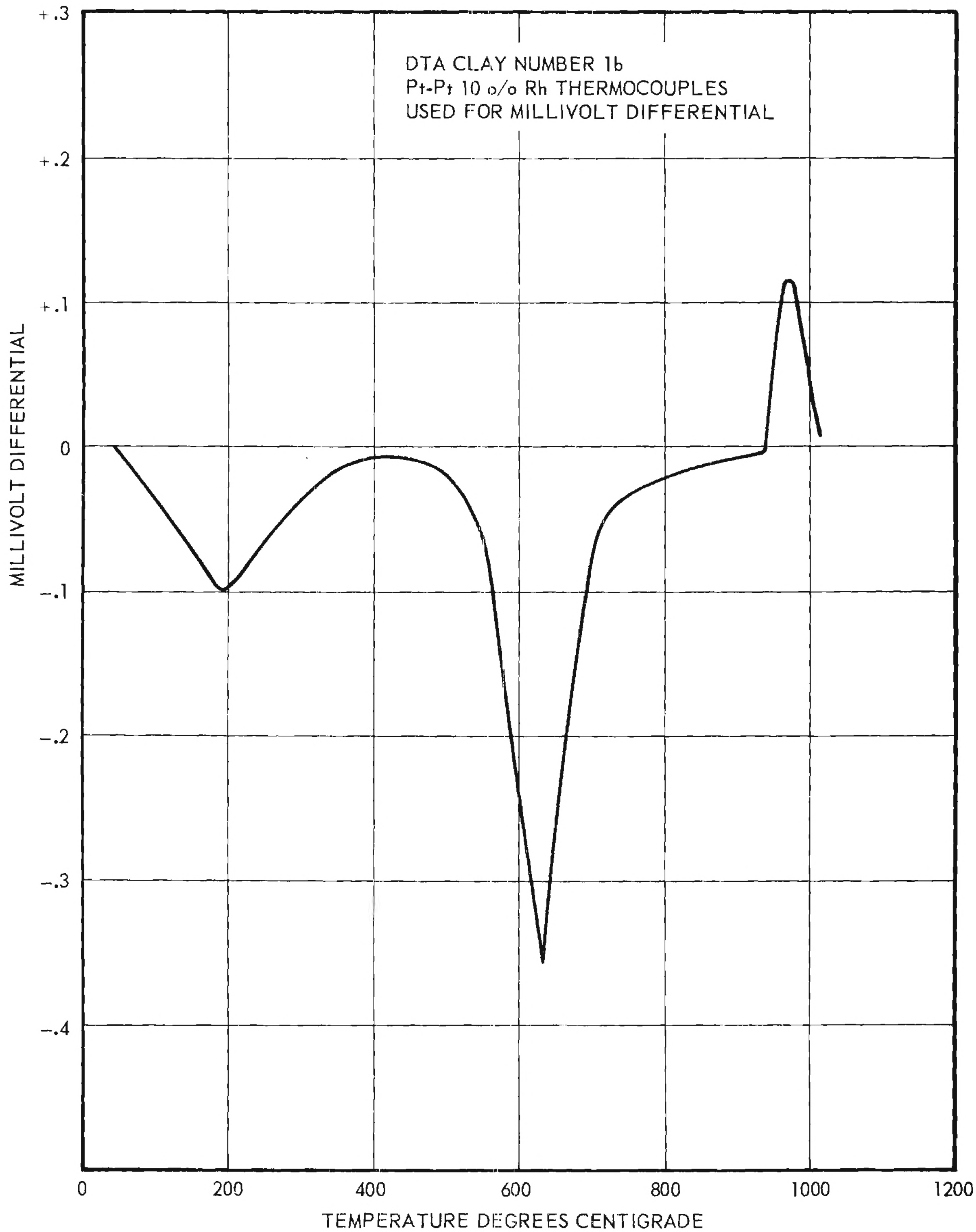


Figure 10a. Differential Thermal Analysis Curve for Clay 1-b.

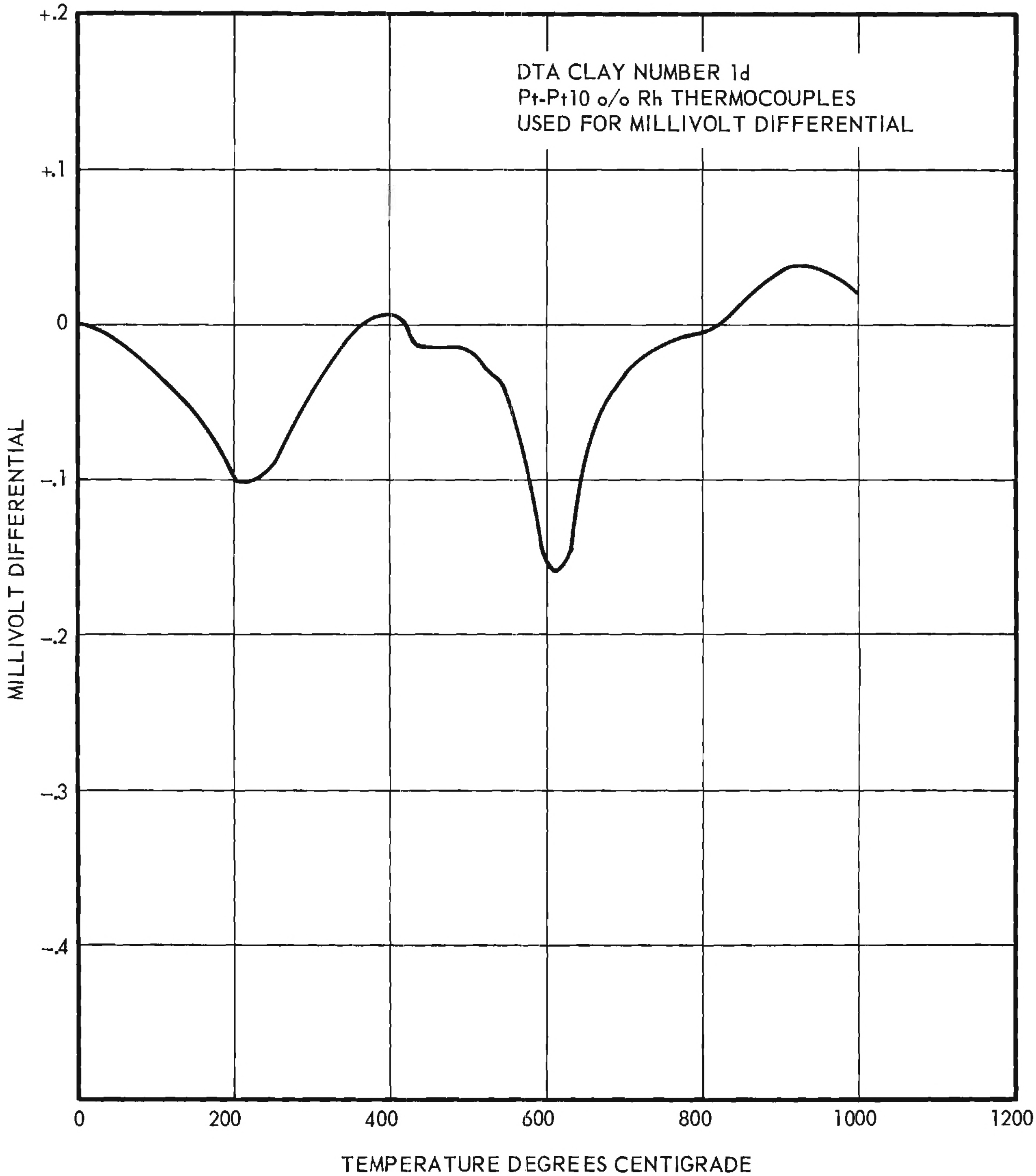


Figure 10b. Differential Thermal Analysis Curve for Clay 1-d.

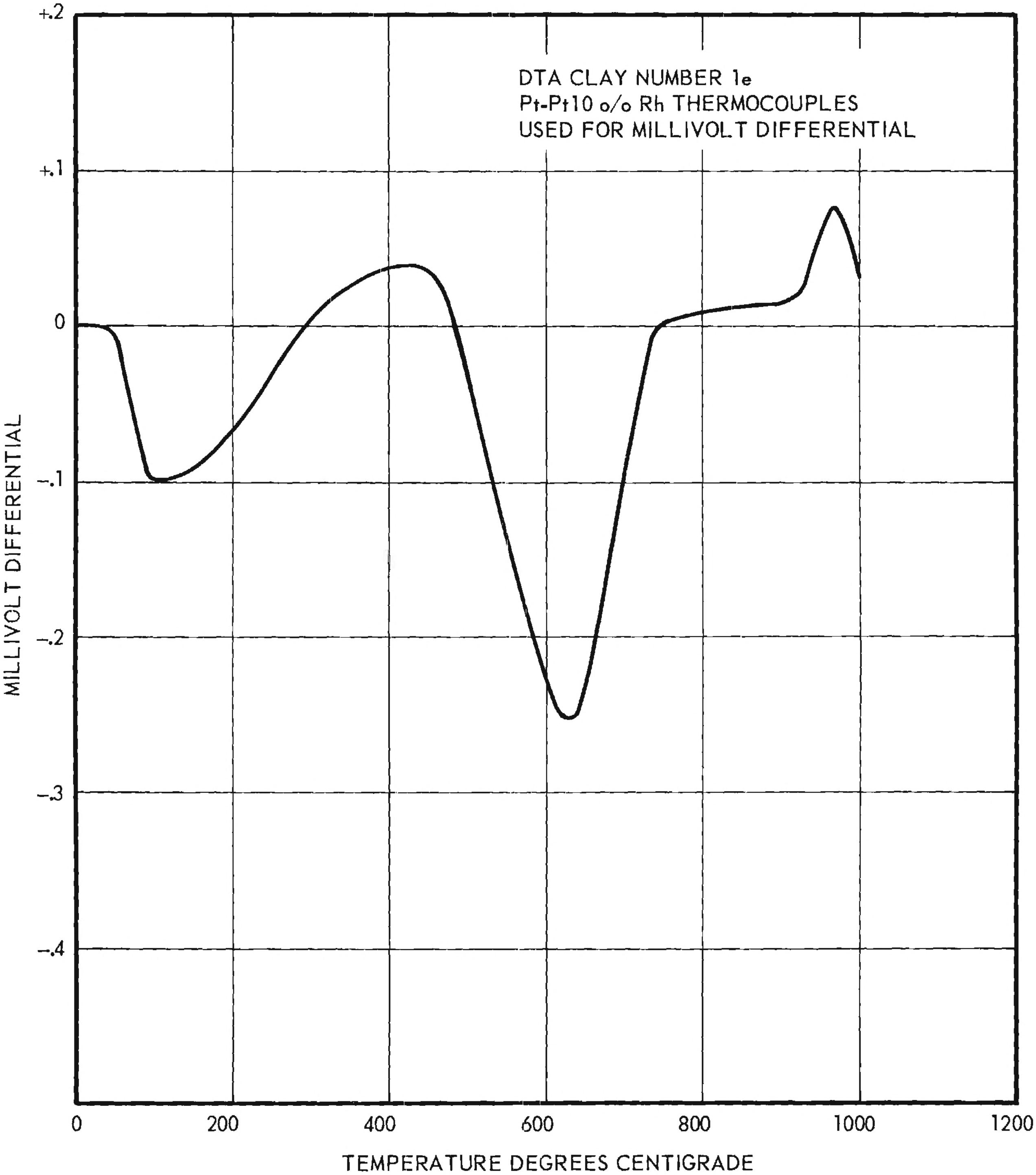


Figure 10c. Differential Thermal Analysis Curve for Clay 1-e.

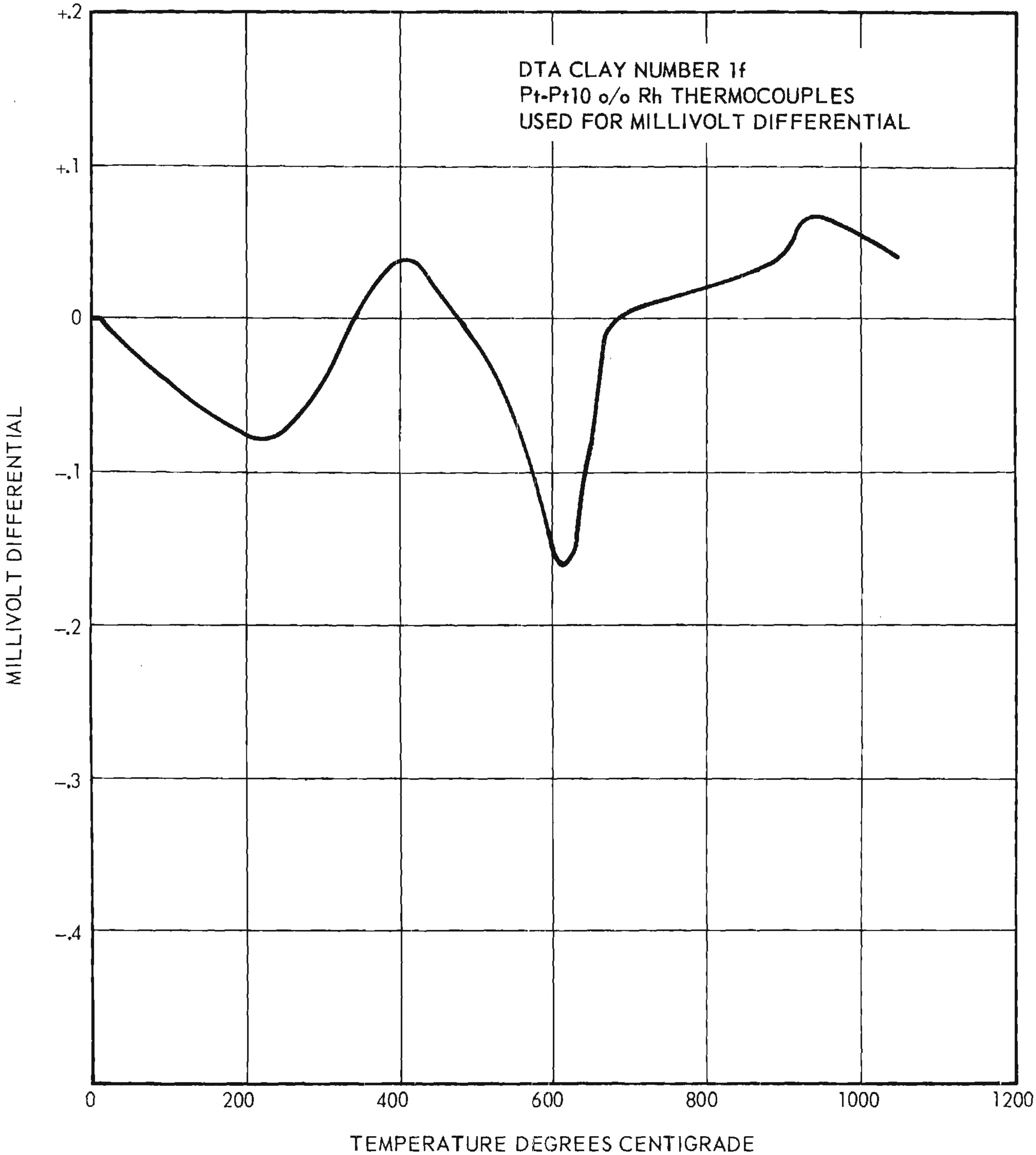


Figure 10d. Differential Thermal Analysis Curve for Clay 1-f.

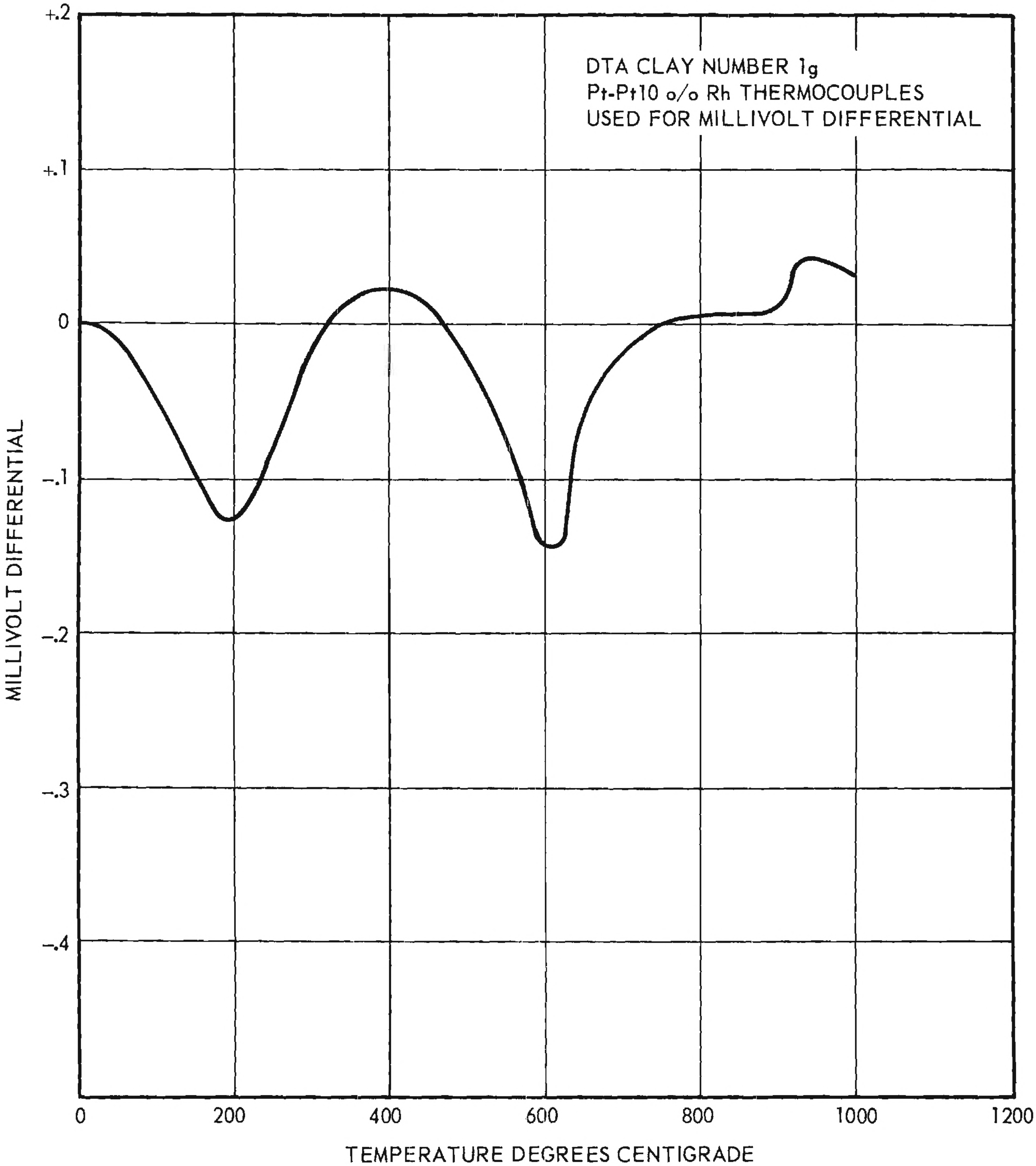


Figure 10e. Differential Thermal Analysis Curve for Clay 1-g.

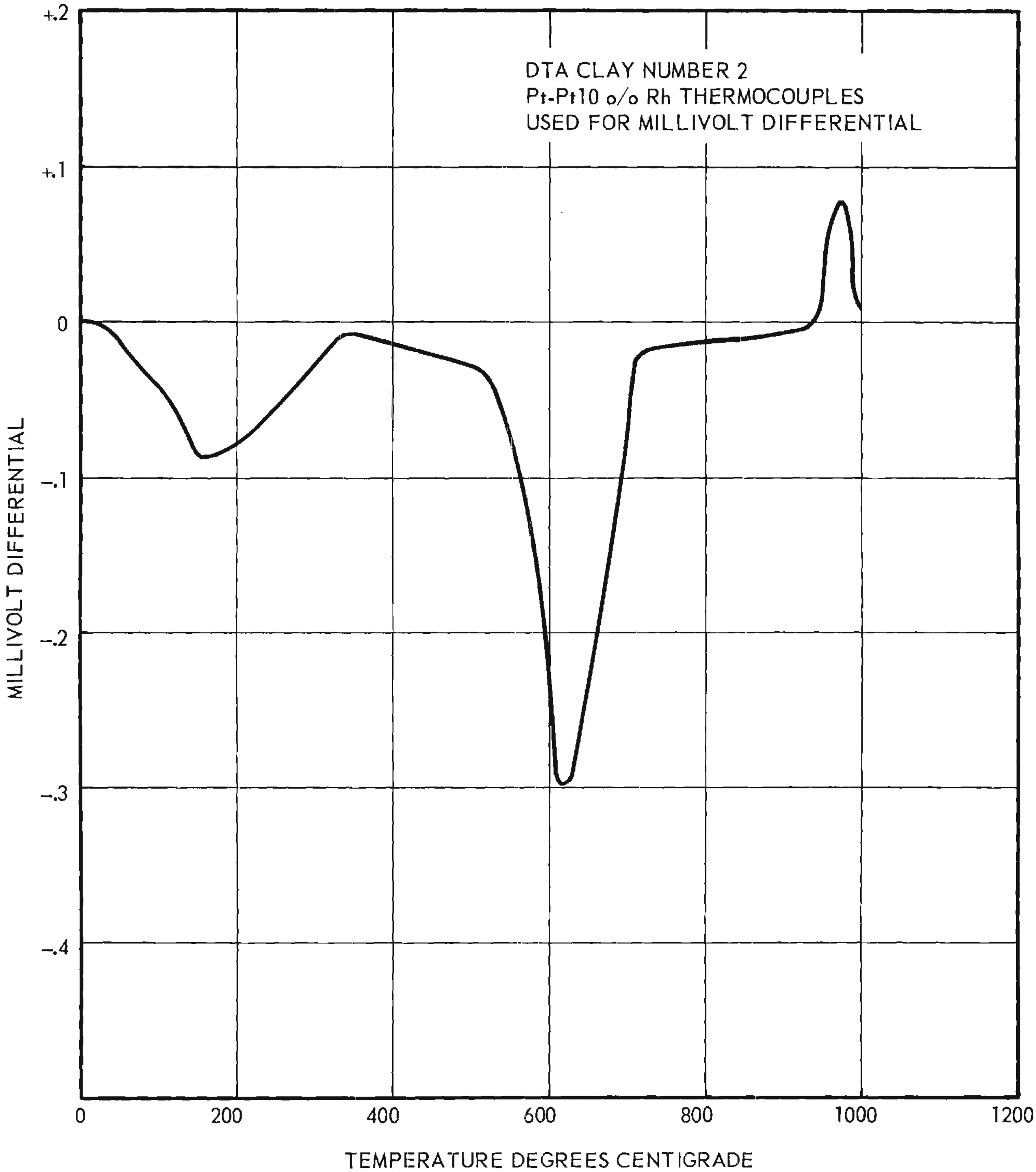


Figure 10f. Differential Thermal Analysis Curve for Clay 2.

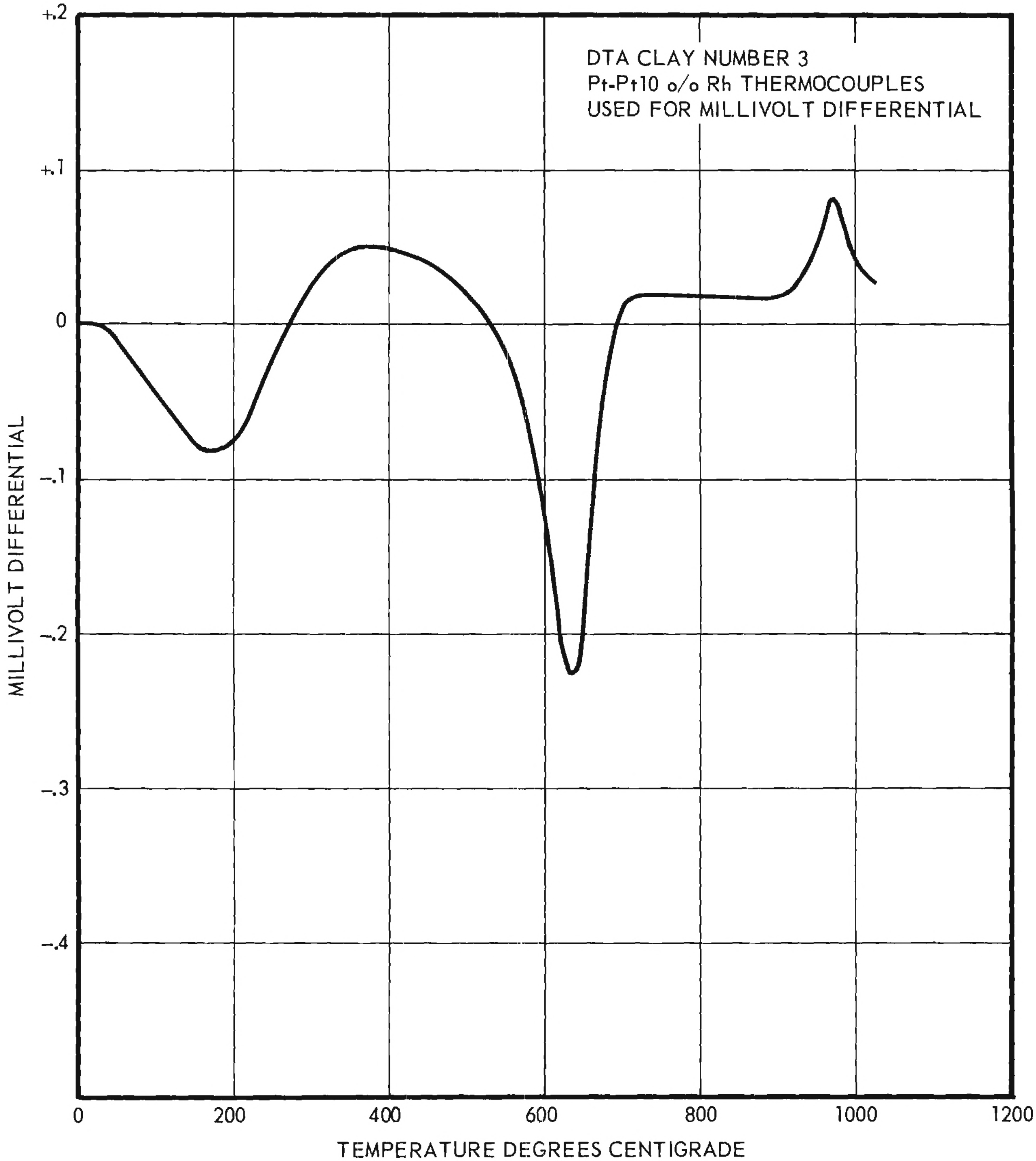


Figure 10g. Differential Thermal Analysis Curve for Clay 3.

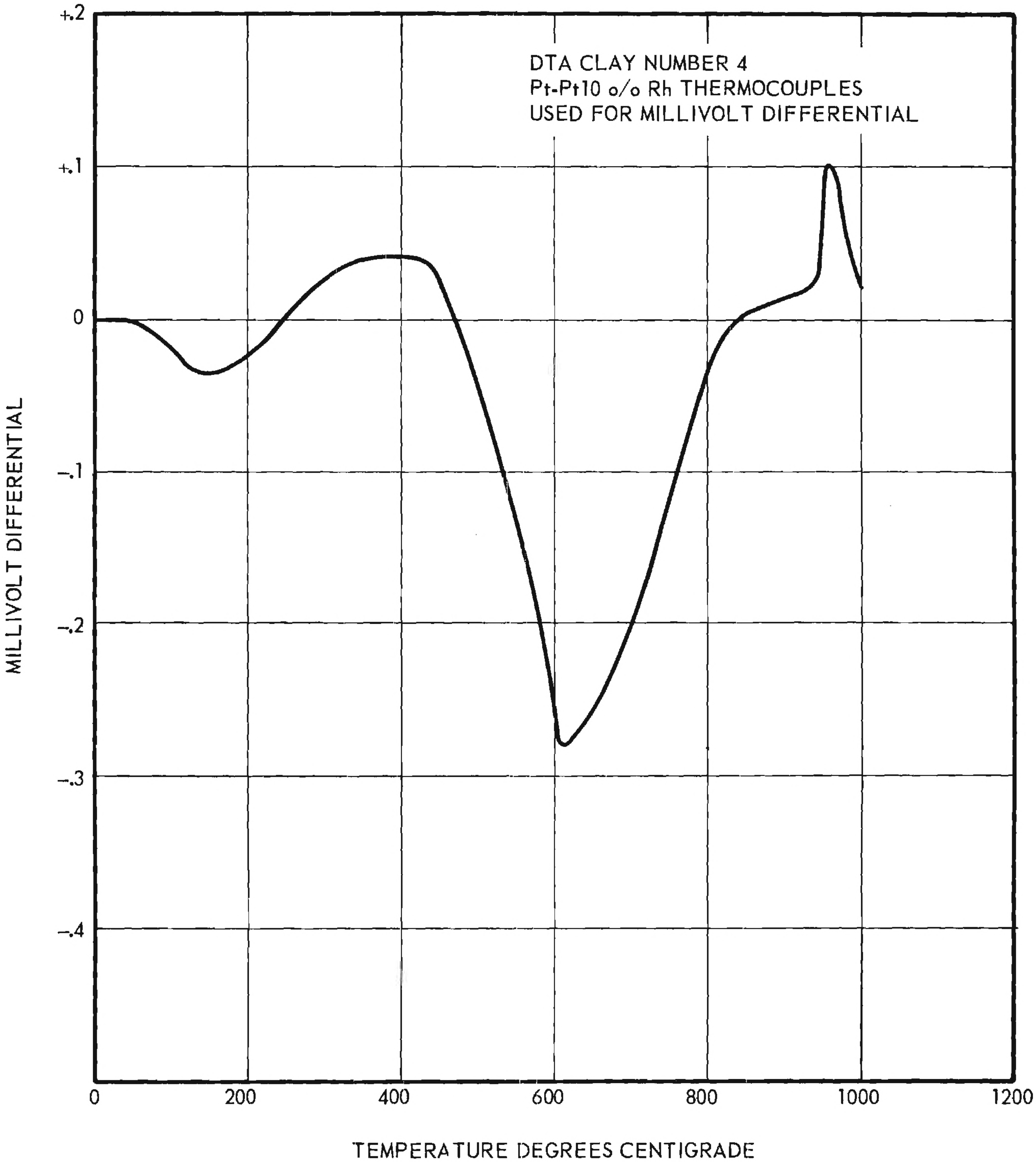


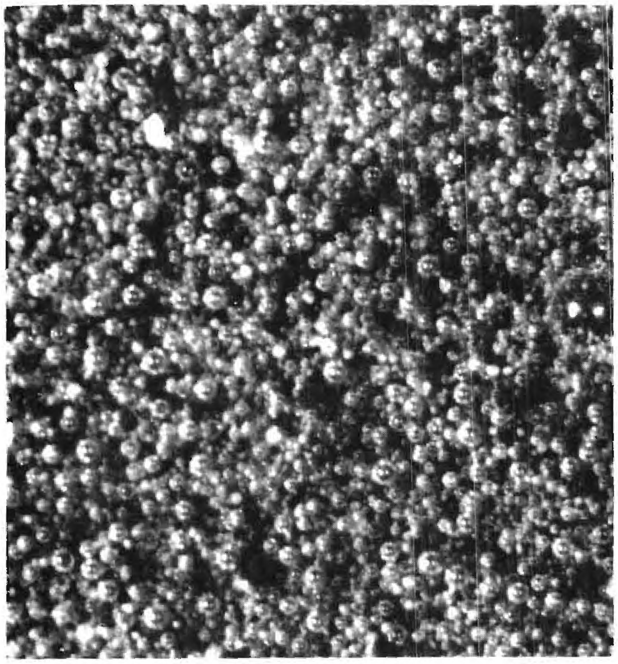
Figure 10h. Differential Thermal Analysis Curve for Clay 4.

4 parts	Silica
1/2 part	Borax
1/8 part	Bentonite
1/8 part	Magnesium Carbonate
50 parts	Water

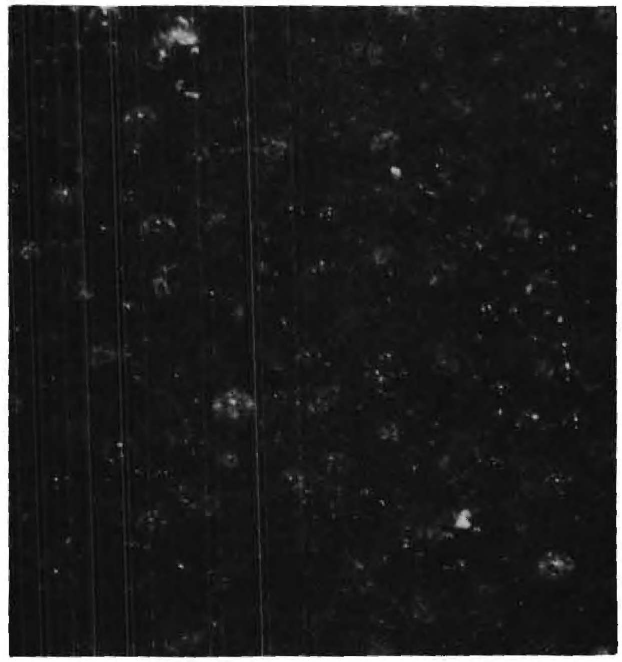
Steel samples coated were C1012 steel plates 4" x 4" x 3/16". All samples were fired in an inconel firing chamber with an atmosphere provided by passing air through water at 25°C. All samples were fired for 22 minutes at 1375°F. The bubble stratum of each plate was then examined under an 80 power binocular microscope. Photomicrographs of the bubble structure of enamels made with each of the eight clays appear in Figure 11. Table IX shows the number of bubbles per square inch and the average size of each bubble in the bubble strata. No apparent relationship can be found between the chemical water contained in a clay and the size and number of bubbles in the bubble strata of an enamel made with the clay. However, the enamels made with the clays containing the greatest amount of chemical water had the least minute fishscale defects. Generally it was found that the better crystallized clays had the greater chemical water content. The relative crystallinity of a clay may be determined from the differential thermal analysis curve. Those clays exhibiting a sharp chemical water peak and alumina transformation peaks (980°C) are considered to have the best crystallinity.

3. Reagent - Alumina

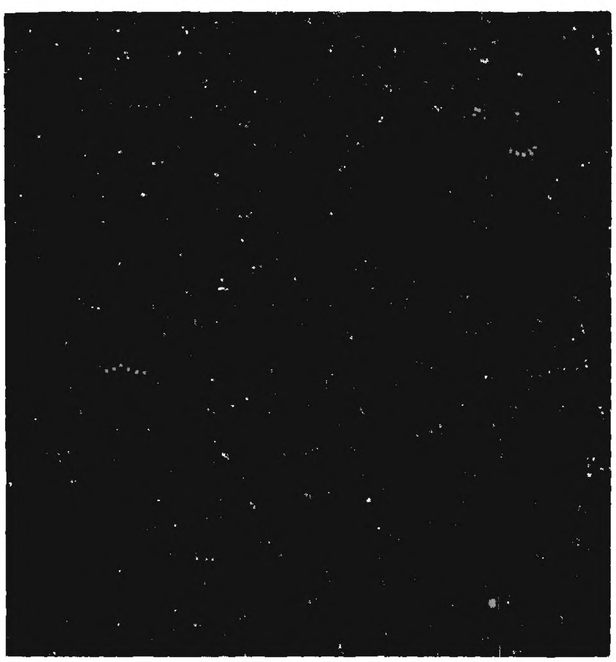
The single grade of alumina used was an 80 mesh fused alumina and was added before milling to the standard mill batch in a concentration of 10 parts fused alumina to 100 parts frit. The study of alumina bearing



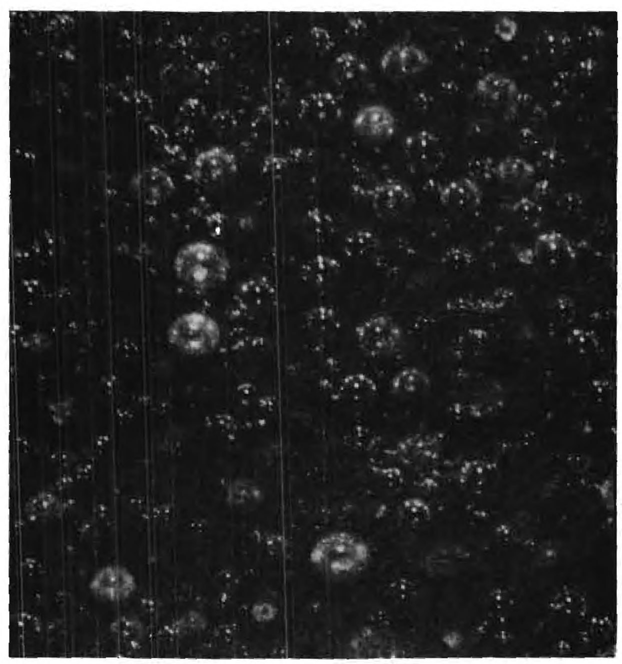
(a) CLAY 1-b



(b) CLAY 1-d

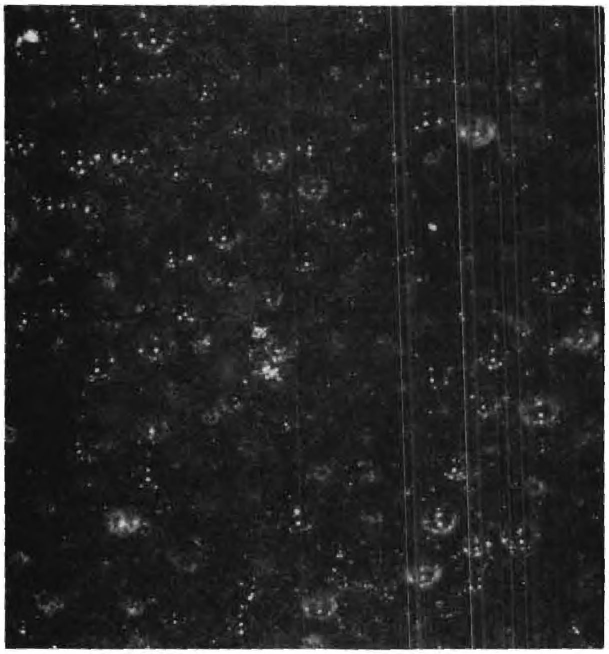


(c) CLAY 1-e

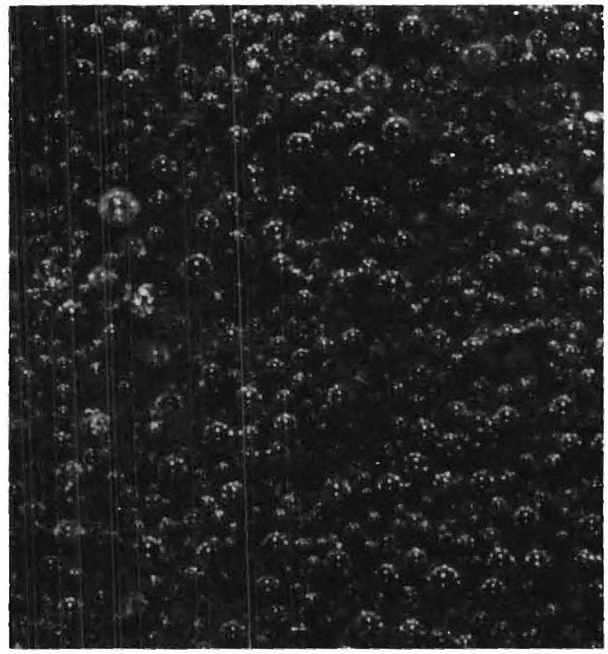


(d) CLAY 1-f

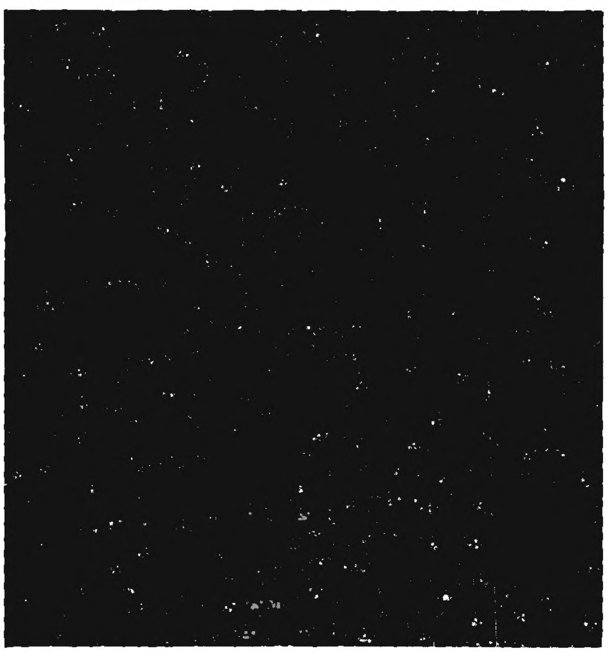
Figure 11. Photomicrographs of Bubble Stratum of -S- Enamel Prepared with Various Enameling Clays. (60X)



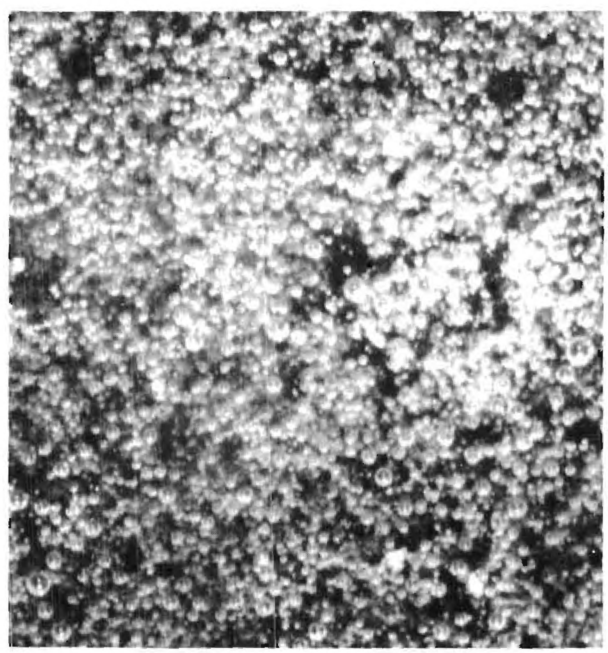
(e) CLAY 1-g



(f) CLAY 2



(g) CLAY 3



(h) CLAY 4

Figure 11 (Continued). Photomicrographs of Bubble Stratum of -S- Enamel Prepared with Various Enameling Clays. (60X) enamels was limited to gas extraction studies so that a greater portion of project time could be devoted to qualification of steel plate.

TABLE IX

BUBBLE SIZE AND NUMBER OF BUBBLES PER SQUARE INCH IN BUBBLE STRATA OF STANDARD ENAMEL

	Bubble Size			
Clay	Maximum in.	Minimum in.	Average in.	Number of Bubbles Per in^2
1b	3.8×10^{-3}	3.9×10^{-4}	1.60×10^{-3}	1.36×10^{5}
1d	4.5×10^{-3}	3.5×10^{-4}	1.45×10^{-3}	1.39×10^{5}
1e	2.8×10^{-3}	5.2×10^{-4}	1.28×10^{-3}	2.82×10^{5}
1f	5.6×10^{-3}	3.3×10^{-4}	1.54×10^{-3}	1.32×10^{5}
1g	4.5×10^{-3}	1.9×10^{-4}	1.45×10^{-3}	1.39×10^{5}
2	3.8×10^{-3}	2.8×10^{-4}	1.45×10^{-3}	2.22×10^{5}
3	4.3×10^{-3}	4.5×10^{-4}	1.45×10^{-3}	2.48×10^{5}
4	2.1×10^{-3}	2.3×10^{-4}	1.40×10^{-3}	1.24×10^{5}

B. Gas Extraction Crucible Test

Since clay is a naturally occuring material its composition and properties may vary even in the same vein of clay. Previous work has shown that clay is one of the significant variables in establishing a "reagent" porcelain enamel slip to be used in the qualification of steel plate for enameling purposes. To study further the effects of clay additions to the enamel batch and to determine if clay could be eliminated from the enamel batch, a new gas extraction test was devised. This test consisted of placing a 1-1/2- x

2- x 3/16-inch sandblasted steel specimen in a fused silica crucible and completely covering this sample with dry powdered frit or a mixture of powdered frit and clay in the proper proportions for a workable enamel. The crucible was then heated to 840°C in a furnace for 30 minutes and the molten enamel and steel specimen poured from the crucible into water to quench the enamel. Any enamel not shattered from the steel specimens was sandblasted off and the specimens set up in the gas extraction apparatus. The amount of gas given off was determined by a method developed under a previous contract. Crucible tests were run with the following frit blend.

Frit No.	Parts by Weight
S-1	65
S-2	15
S-3	20

For the frit-clay mixture an additional six parts of clay were added.

Tests for introducing gas into steel were run on frit and steel, with and without clay under several different conditions. The crucible and materials were dried under several conditions to determine the effects of adsorbed water, carbonaceous matter and chemical water contained in the frit and clay. The method of drying and the amount of gas extracted after firing the crucibles to 840°C is given in Table X.

Larger amounts of gas were extracted from both the systems containing clay and those not containing clay than is normally extracted from an equivalent sample coated by spraying or dipping in a porcelain enamel slip. This might be attributable to the higher firing temperature and the longer time required by the crucible method to insure that the frit is molten. As the temperature of drying was increased for both the systems containing clay, and those not containing clay, the amount of gas extracted increased up to 350°C (See Figure 12). This may have been due to oxidation of the steel specimen during the drying phase. For the system dried at 620°C there was a decrease in the amount of gas extracted. This might be attributed to the frits becoming quickly molten at this temperature thus keeping oxygen in the furnace atmosphere from coming in contact with the steel specimen.

TABLE X

GAS EXTRACTION DATA OBTAINED FROM CRUCIBLE TEST

Test No.	Material Treatment	Crucible Contained	Gas Extracted: Uncontrolled Atmosphere (Ml)	Gas Extracted: Controlled Atmosphere 1 (Ml)	Gas Extracted: Controlled Atmosphere 2 (Ml)
1	As received No drying	Frit and Steel	0.51	0.56	0.56
1	As received No drying	Frit, Steel and Clay	0.86	0.85	1.05
2	Dried at 110°C for 24 hours	Frit and Steel	0.25	0.20	0.15
2	Dried at 110°C for 24 hours	Frit, Steel and Clay	0.46	0.16	0.46
3	Dried at 175°C for 24 hours	Frit and Steel	0.80	0.70	0.81
3	Dried at 175°C for 24 hours	Frit, Steel and Clay	1.40	1.28	1.40
4	Dried at 350°C for 24 hours	Frit and Steel	0.75	1.40	0.62
4	Dried at 350°C for 24 hours	Frit, Steel and Clay	2.25	1.75	1.95
5	Dried at 620°C for 24 hours	Frit and Steel	0.80	1.00	1.01
5	Dried at 620°C for 24 hours	Frit, Steel and Clay	1.06	0.80	0.81

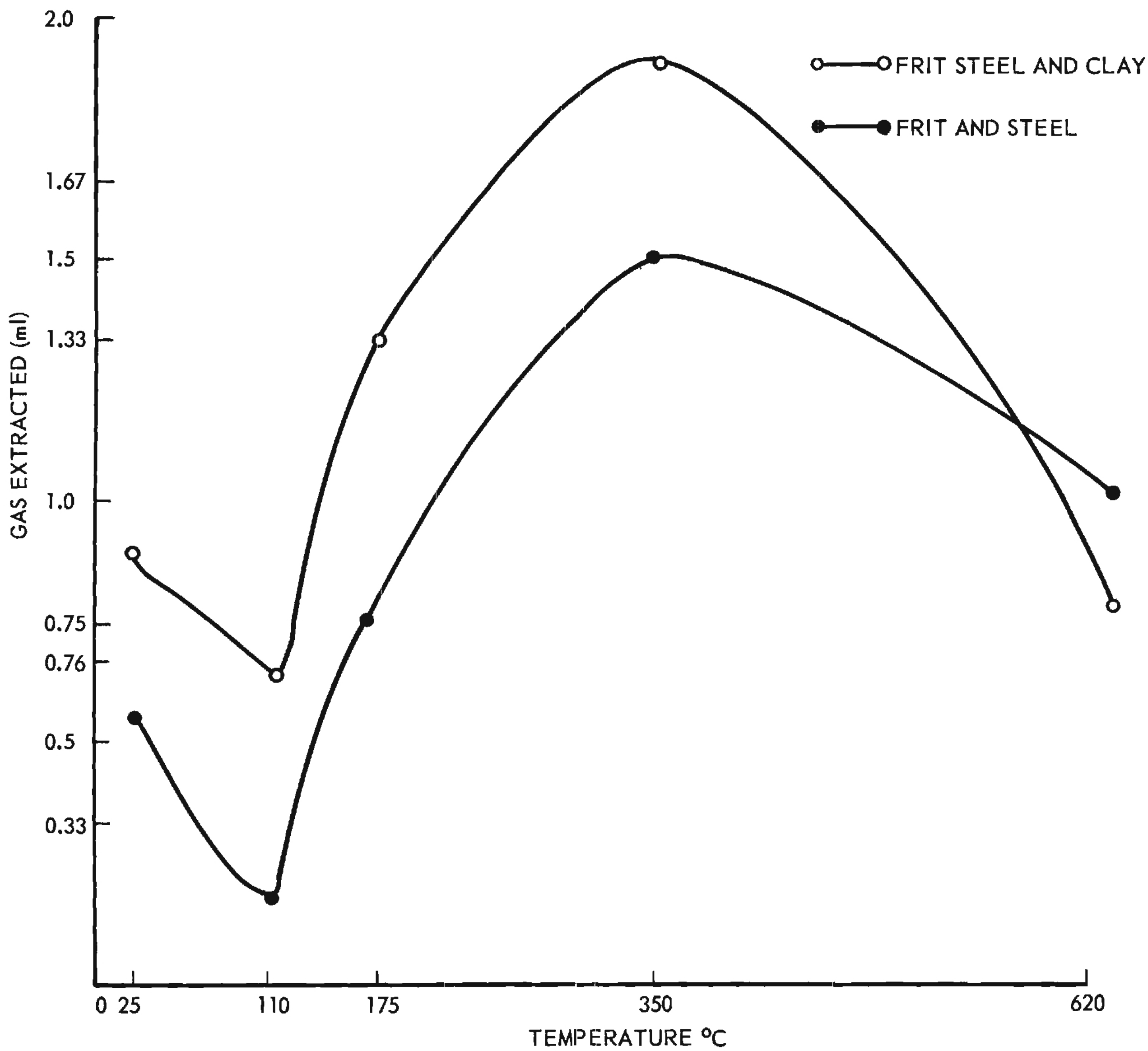


Figure 12. Effect of Drying on Gas Extraction Crucible Test.

C. Quenching Mediums for Gas Extraction Specimens

The use of a quenching medium other than water was considered due to the possibility of injecting hydrogen into the steel while the specimen is being quenched in water.

To observe the rate of cooling of C 1012 steel blanks coated with -S- Enamel when quenched in liquid nitrogen, still air, and water, the following procedure was used.

Chromel and alumel wires were spot welded to the center of one side of a 1-1/2- x 2- x 3/16-inch C 1012 steel blank. The wires were welded 1/4-inch apart. The sample was then coated with -S- Enamel by dipping and allowed to dry. The thermocouple was connected to a strip chart recorder. The coated steel blank was placed in a furnace at 746°C for 12 minutes and then removed and plunged immediately into the quenching medium. Two samples were run for each quenching medium. The cooling curves obtained are shown in Figure 13. The enamel coating on the sample cooled in air and the enamel coating on the sample cooled in liquid nitrogen remained in good condition while the coatings on the water quenched samples were severely thermal shocked and cracked off the metal. It is believed that the larger amount of gas extracted from water-quenched samples is due to the quicker cooling action which impedes diffusion and thereby entraps gas in the metal. The slow cooling of the metal in liquid nitrogen is believed to result from the insulating effect of the nitrogen gas envelope formed around the hot metal sample; therefore, it is believed that such quenching mediums as liquid nitrogen and solid carbon dioxide would not be suitable for gas extraction samples. It is felt that quick cooling of the samples is necessary to retain as much gas as possible. Therefore, the use of water as a quenching medium was adopted.

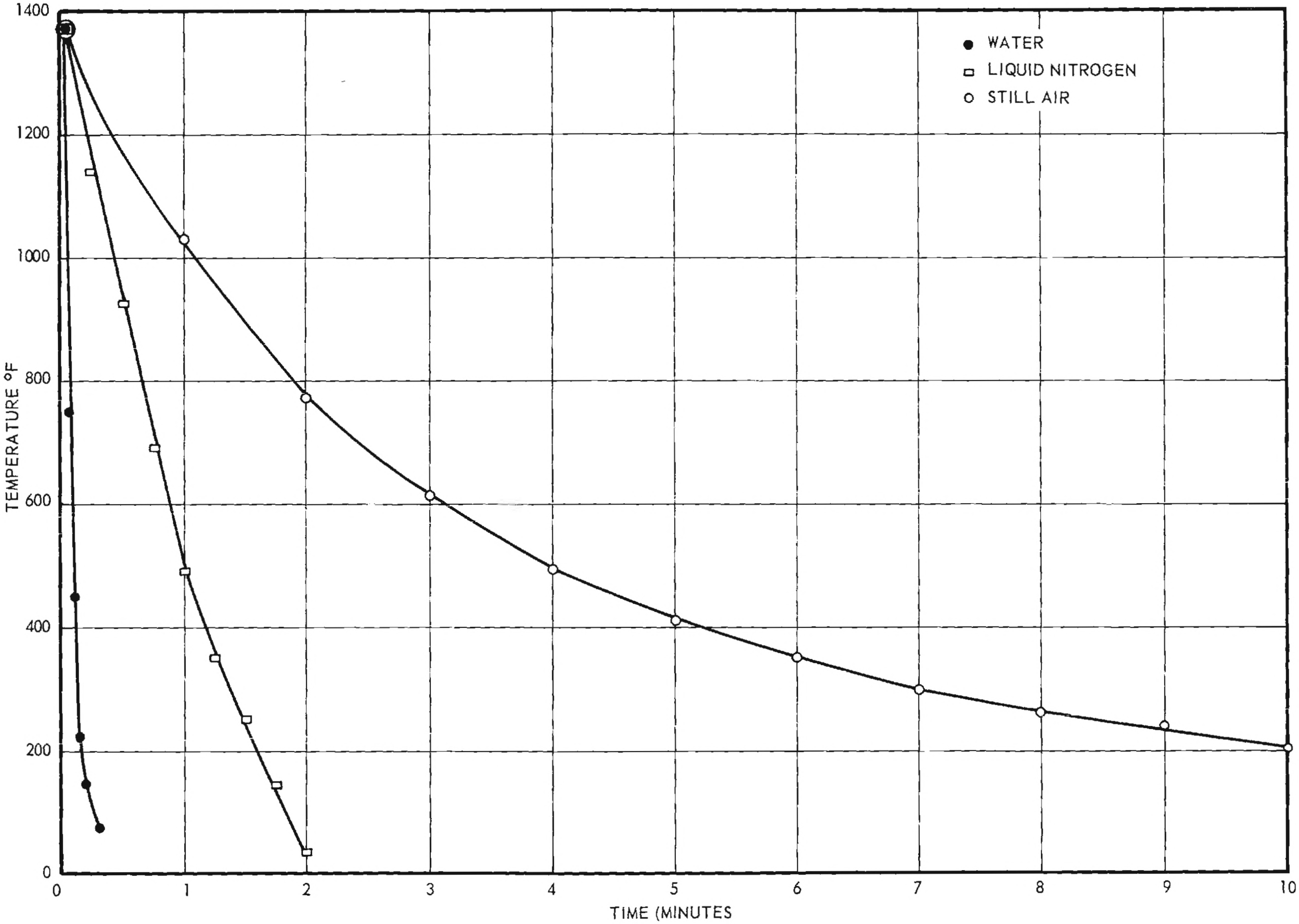


Figure 13. Cooling Curves for Quenching of Gas Extraction Samples.

D. Qualification of Steel Plate

As a result of the work under previous contracts a tentative procedure for qualification of steel plate for enameling purposes was suggested. Samples of steel cut from each plate would be enameled with a "standard qualifying enamel" and subjected to the following studies: (1) extractable gas, (2) accelerated fishscale observations, and (3) spalling (thermal quench) studies. Four possible cases could arise using these tests. These cases are outlined below.

Case I - Extractable gas, satisfactory (low)
Accelerated fishscale, Negative (No fishscale)
Spalling, None
Material acceptable

Case II - Extractable gas, excessive
Accelerated fishscale, negative (No fishscale)
Spalling, none
Of questionable acceptance because high extractable gas, no spalling tendency might be cause for negative fishscale result; gas could have been sealed in by enamel. In this case the accelerated fishscale test on the quenched spalling test specimens would be re-run. If the accelerated fishscale remains negative the steel plate would be acceptable.

Case III- Extractable gas, satisfactory
Accelerated fishscale, positive
No need to run spalling; plate rejected.

Case IV - Extractable gas, satisfactory

Accelerated fishscale, negative

Spalling, positive

Material would be unacceptable because steel is insufficiently reactive to bond well with the enamel.

To determine if this system could be used to qualify steel plate acceptably receptive to porcelain enamel coatings, a large variety of steel plate was needed. The leading steel manufacturers were invited to submit samples of steel plates for this study. Eight 3/16-inch thick and four 1/4-inch thick steel plates were received from the various manufacturers. The pertinent information supplied with each of the plates can be found in Table XI. The following size specimens were cut from each steel plate, 4- by 4-inch, 4- by 8-inch and $1\frac{1}{2}$- x 2-inch. All specimens were cleaned by sandblasting and were coated by spraying with the standard enamel listed on page 27.

After slip coating, all specimens were allowed to dry in a 60°C oven to form the bisque. Firing temperature of all bisque coated specimens was 1375°F. Specimens 3/16 inch thick were fired 22 minutes. Specimens 1/4 inch thick were fired 27 minutes. All samples were fired in an inconel chamber in which a moist atmosphere was maintained during firing by passing air through water at 25°C into the inconel chamber at a rate of eight liters per minute.

1. Gas Extraction

Twelve 1-1/2- by 2-inch specimens were cut from each steel plate, coated with -S- Enamel and fired at 1375°F after which, each was quenched by immersing in room temperature water. Any coating remaining after quenching was removed by sandblasting. The samples were immediately set up in the gas extraction apparatus (Figure 14) and heated to 175°C for 4 hours. The amount of gas extracted was measured and recorded. The gas extraction values obtained for each of the steels is listed in Table XII.

The gas extraction procedure was repeated on all steels using -S- Enamel containing 10 parts fused alumina added as a mill addition. The results of this study appear in Table XIII. Figures 15a and b show the effect of carbon content on gas extraction specimens coated with alumina free and alumina bearing -S- Enamel. It can be seen that gas extraction curves for specimens coated with both enamels reach a maximum around 0.12 per cent carbon. It can also be seen that the addition of alumina tends to modify the extreme amounts of gas extracted from coated specimens.

2. Accelerated Fishscale Observations

Four 4- by 4-inch plates from each steel were coated with -S- Enamel fired and cooled in air to room temperature. Firing times were the same as for gas extraction specimens. The samples were observed for fishscale and then placed in a 175°C oven. After 24 hours the samples were removed and observed for fishscale. The samples were then placed in a 225°C oven for an additional 24 hours after which time they were again observed for fishscale. In order to give some idea of the amount of fishscale appearing on the surface of a plate, measurements are reported as average fishscale per square centimeter for surface chipping sometimes referred to as shiner scale.

If large fishscale appeared on the plate, the number and size of the imperfections appearing on the 4- by 4-inch plate is reported. Table XIV and Figure 16 show the data collected on fishscale observation.

HEAT HISTORY AND CHEMICAL COMPOSITION
OF STEEL PLATES

Steel	C	Mn	P	S	Si	Cu	Ni	CR	Other	Yield Point	Tensile Strength	Elongation 8"	
T	0.11	0.46	0.017	0.028	0.10	0.06	0.08	0.01	0.003	38,900	55,100	28	Killed, hot topped, top poured heat for enameling quality plates under ASTM-A285-57T. Ingot rolled into 5 inch thick by 52 inch wide slabs which were reheated, cross rolled to approximately 80 inches wide (about 50% cross rolling) and then straight rolled to 3/16 inch thickness.
J-1	0.26	0.49	0.013	0.032						46,830	71,640	27	Silicon Semi-killed Rolled to .188 x 90 cross rolled
J-2	0.17	0.41	0.011	0.028									Silicon Semi-killed Rolled to .188 x 48 x 296 - straight away
H	0.03	0.08	0.0007	0.020									Porcelain enamel sheets 3/16 in. thick pickled commercial quality
L-1	0.13	0.44	0.010	0.022						39,200	55,400	29.5	A285-57T Grade B Flange 3/16 in.
L-2	0.11	0.44	0.013	0.028	0.20					44,000	63,200	31	A-201-57T Grade A Silicon Killed Flange 3/16 in.
L-3	0.10	0.44	0.018	0.036	0.23		2.30			56,000	76,100	26	A-203-56 Grade B Nickel Flange 3/16 in.

Table XI (Continued)

HEAT HISTORY AND CHEMICAL COMPOSITION OF STEEL PLATES

Steel	C	Mn	P	S	Si	Cu	Ni	CR	Other	Yield Point	Tensile Strength	Elonga-tion 8"	Processing Record
			Chemical Composition (Percent)										
N-1	0.12	0.51	0.013	0.031	0.05				Al 0.028				Semi-killed 1/4 inch
N-2	0.19	0.52	0.017	0.032									Rimmed steel 3/16 inch
W-1	0.12	0.42	0.010	0.021	0.004								1/4 inch
W-2	0.16	0.35	0.010	0.29	0.045								1/4 inch
W-3	0.18	0.45	0.019	0.021	0.22								1/4 inch

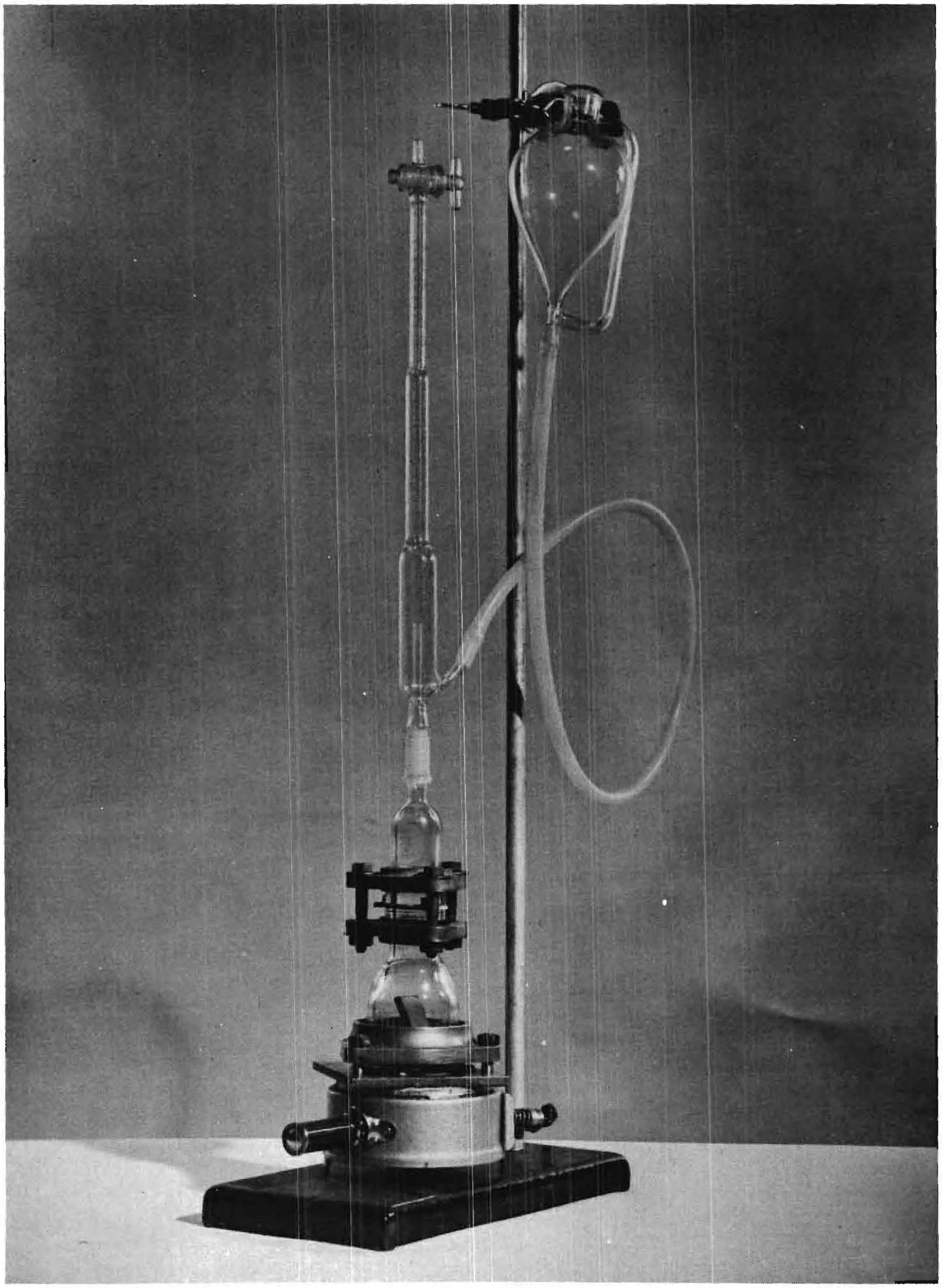


Figure 14. Gas Extraction Apparatus.

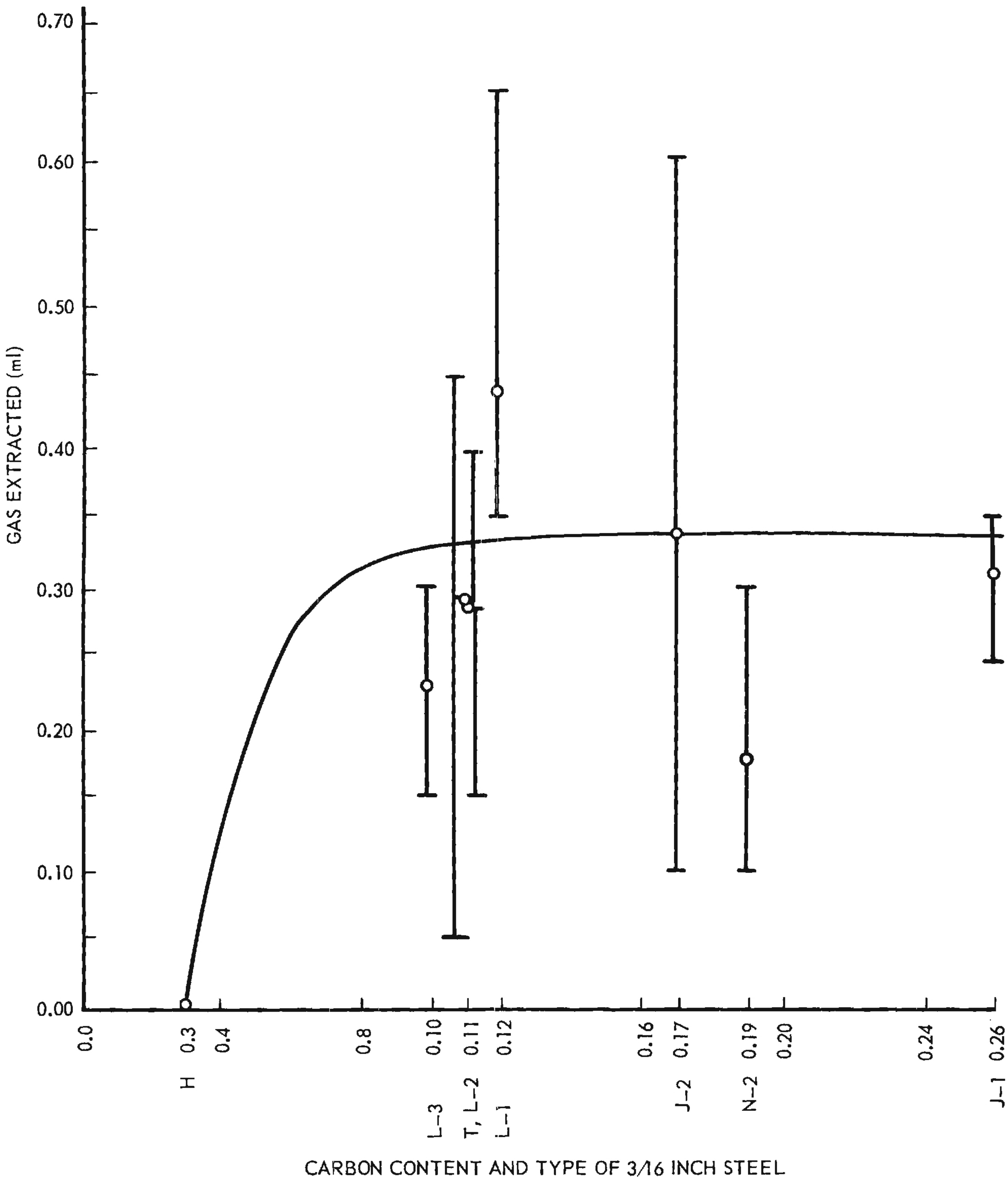
TABLE XII

GAS EXTRACTION VALUES
USING -S- ENAMEL

Steel	Thickness	SAMPLE NO.												
		1 (ml)	2 (ml)	3 (ml)	4 (ml)	5 (ml)	6 (ml)	7 (ml)	8 (ml)	9 (ml)	10 (ml)	11 (ml)	12 (ml)	Avg. (ml)
H	3/16	0	0	0	0	0	0	0	0	0	0	0	0	0
J-1	3/16	0.30	0.30	0.35	-	0.25	0.30	0.35	0.30	0.35	0.30	0.35	0.30	0.31
J-2	3/16	0.35	0.40	0.40	0.35	0.35	0.35	0.45	0.15	0.20	0.10	.60	0.25	0.33
L-1	3/16	0.35	0.35	0.40	0.40	0.35	0.35	0.40	0.65	0.50	0.55	0.45	0.35	0.43
L-2	3/16	-	0.15	0.25	0.15	0.25	0.20	0.40	0.35	0.35	0.30	0.40	0.30	0.28
L-3	3/16	-	0.20	0.20	0.15	0.20	0.20	-	0.25	0.30	0.30	0.25	0.25	0.23
N-1	1/4	0.15	0.15	0.20	0.15	0.15	0.15	0.30	0.20	0.20	0.15	0.40	0.15	0.20
N-2	3/16	0.10	0.15	0.15	0.10	0.10	0.10	0.20	0.30	0.25	0.25	0.30	0.20	0.18
T	3/16	0.35	0.35	0.35	0.35	0.05	0.30	0.38	0.25	0.20	0.25	0.20	0.45	0.29
W-1	1/4	0.85	0.20	0.25	0.15	0.20	0.15	0.20	0.15	0.35	0.25	0.15	0.45	0.28
W-2	1/4	0.15	0.60	0.65	0.60	0.25	0.30	-	0.20	0.25	0.20	0.30	0.30	0.35
W-3	1/4	0.20	0.15	0.25	0.20	0.25	0.20	0.20	0.20	0.20	0.20	0.45	0.20	0.23

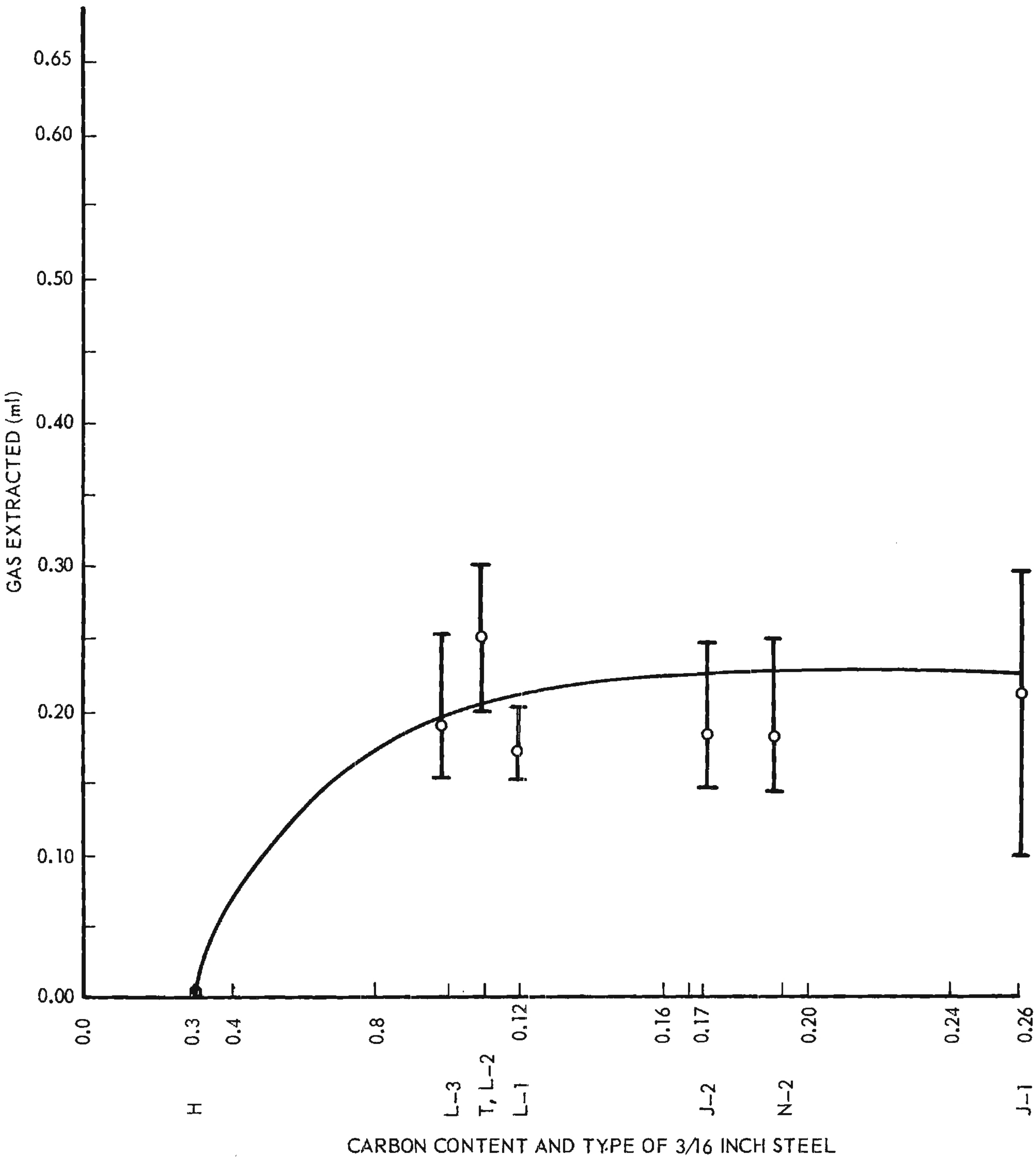
3. Spalling

For this test a T-joint specimen described in Specification MIL-P-16961B is used. This specimen consists of a 4- by 4- by 5/8-inch metal section butt welded at right angles to and at the mid-length of a 4- by 8-inch by 3/16-inch section (See Figure 17). The T-joint is sandblasted enameled and subjected to the thermal shock test described in 4.5.2.1 of MIL-P-16961B. This test consists of quenching the T-joint by immersion in water 5 times from a temperature



(a) GAS EXTRACTED VERSUS CARBON CONTENT FOR 3/16 INCH STEELS COATED WITH -S- ENAMEL.

Figure 15. Gas Extracted Studies.



(b) GAS EXTRACTED VERSUS CARBON CONTENT FOR 3/16 INCH STEELS COATED WITH -S- ENAMEL +10% ALUMINA.

Figure 15 (Continued). Gas Extracted Studies.

of 650°F, 5 times from 800°F and 5 times from 900°F. An alternate spalling test consists of placing a 4- by 8- inch section of enameled metal on a spray-quench box so that a 4- by 4-inch section of one side of the enameled plate is subjected to a spray of tap water (See Figure 18). Samples are quenched five times at each of the temperatures used with the T-joints. The occurence of a crack, chip or other defect which causes exposure of the base metal except within a distance of 1/8-inch of the plate edges shall be cause for rejection.

TABLE XIII

GAS EXTRACTION VALUES
USING -S- ENAMEL CONTAINING
TEN PER CENT FUSED ALUMINA

Steel	Thickness (inches)	SAMPLE NO. 1 (ml)	2 (ml)	3 (ml)	4 (ml)	5 (ml)	6 (ml)	Average (ml)
H	3/16	0	0	0	0	0	0	0
J-1	3/16	0.25	0.25	0.30	0.10	0.15	0.25	0.21
J-2	3/16	0.15	0.15	0.20	0.15	0.25	0.20	0.18
L-1	3/16	0.15	0.20	0.20	0.15	0.20	0.15	0.17
L-2	3/16	0.25	0.20	0.30	0.25	0.25	0.25	0.25
L-3	3/16	0.20	0.15	0.25	0.20	0.15	0.15	0.18
N-1	1/4	0.25	0.20	0.30	0.15	0.25	0.20	0.23
N-2	3/16	0.15	0.15	0.25	0.15	0.20	0.20	0.18
T	3/16	0	0	0	0	0	0	0
W-1	1/4	0.25	0.25	0.25	0.30	0.30	0.30	0.27
W-2	1/4	0.25	0.20	0.25	0.25	0.20	0.25	0.23
W-3	1/4	0.25	0.25	0.25	0.30	0.30	0.25	0.27

ACCELERATED FISHSCALE STUDIES

STEEL	SPECIMEN NUMBER	CARBON CONTENT (%)	STEEL THICKNESS (INCHES)	THICKNESS OF COATING (MILS)	FISHSCALE ROOM TEMP.	FISHSCALE 24 HOURS 175°C	FISHSCALE 24 HOURS 225°C	AVERAGE GAS EXTRACTED (ML)
H	1	0.03	3/16	3.5	0	0	0	0.00
	2			3.0	0	0	0	
	3			4.0	0	0	0	
	4			7.0	0	0	0	
J-1	1	0.26	0.188	8.0	Average of 6 large fishscale on each side of each 4x4 plate	——	——	0.31
	2			6.0				
	3			6.0				
	4			5.5				
J-2	1	0.33	0.188	5.0	0	0	0	0.33
	2			5.0	0	0	0	
	3			7.0	0	0	0	
	4			5.0	0	0	0	
L-1	1	0.13	3/16	3.0	3 small fish-scale/cm^2	No Change	No Change	0.42
	2			4.0	0	0	0	
	3			5.0	0	0	0	
	4			5.0	0	0	0	
L-2	1	0.11	3/16	5.0	0	0	0	0.28
	2			5.0	0	0	0	
	3			7.0	0	0	0	
	4			7.0	0	0	0	
L-3	1	0.10	3/16	6.0	0	0	0	0.23
	2			6.0	0	0	0	
	3			8.0	0	0	0	
	4			7.0	0	0	0	
N-1	1	0.12	1/4	4.0	15 small fish-scale/cm^2	No Change	No Change	0.20
	2			4.0	12 "			
	3			4.0	13 "			
	4			4.0	14 "			
N-2	1	0.19	3/16	4.0	13 small fish-scale/cm^2	No Change	No Change	0.18
	2			4.0	3 "			
	3			2.0	12 "			
	4			3.0	9 "			

ACCELERATED FISHSCALE STUDIES

STEEL	SPECIMEN NUMBER	CARBON CONTENT (%)	STEEL THICKNESS (INCHES)	THICKNESS OF COATING (MILS)	FISHSCALE ROOM TEMP.	FISHSCALE 24 HOURS 175°C	FISHSCALE 24 HOURS 225°C	AVERAGE GAS EXTRACTED (ML)
T	1	0.11	3/16	4.0	0	0	0	0.29
	2			6.0	0	0	0	
	3			7.0	0	0	0	
	4			8.0	0	0	0	
W-1	1	0.12	1/4	8.0	0	0	1 small fishscale/cm^2	0.28
	2			7.0	0	0	0	
	3			8.0	0	0	0	
	4			8.0	0	0	0	
W-2	1	0.16	1/4	4.0	2 fishscale 1/8"	Fishscale 5/cm^2	Fishscale increased in size and exposed bare metal	0.35
	2			4.0	2 "	3/cm^2		
	3			5.0	2 "	3/cm^2		
	4			5.0	1 "	2/cm^2		
W-3	1	0.18	1/4	4.0	0	0	0	0.23
	2			4.0	0	0	0	
	3			2.0	0	0	0	
	4			3.0	0	0	0	

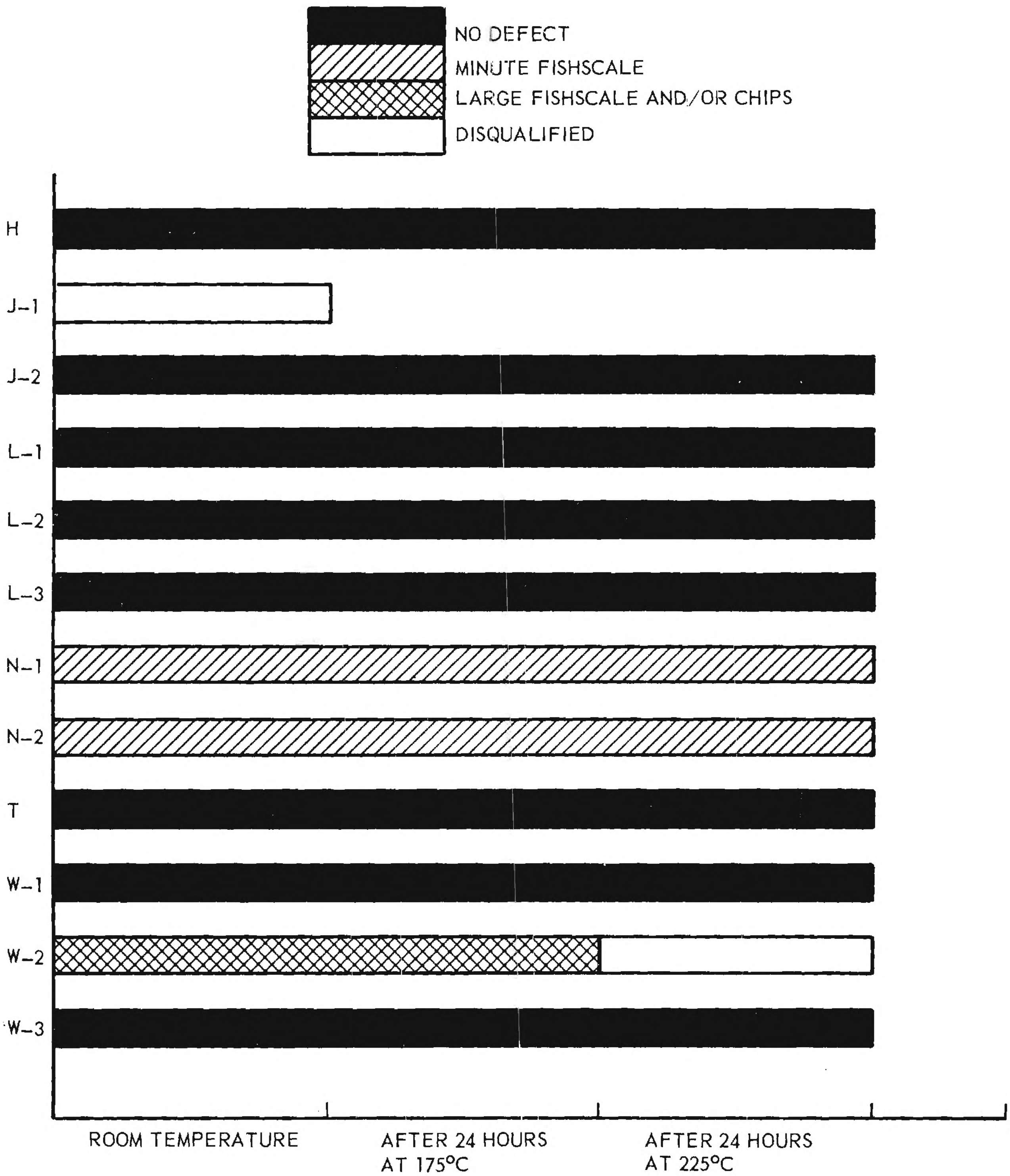


Figure 16. Accelerated Fishscale Studies on Steel Plates Coated with -S- Enamel.

Two T-joints and four 4- by 8- by 3/16-inch specimens from each 3/16 inch steel plate along with four 4- by 8- by 1/4-inch specimens from each 1/4-inch plate were coated with -S- Enamel. The T-joints and one 4- by 8-inch specimen from each of the steels coated with -S- Enamel were subjected to the previously described thermal shock test by immersion in water. Two 4- by 8-inch plates from each steel were subjected to the previously described spray quench test. Results of these studies appear in Tables XV through XVII and in Figures 19 through 21. In both of these quench studies only steel J-1 failed to pass the thermal quench requirements of MIL-P-16961B.

In addition to these studies, one T-joint and one 4- by 8-inch plate from each of the 3/16-inch thick steels and one 4- by 8-inch plate from each of the 1/4-inch steels was shipped to a commercial enameling firm for application of a porcelain enamel coating. One-half of the specimens were coated by dipping and the remaining specimens coated by spraying. The T-joints were thermal shocked by immersion and the 4- by 8-inch plates thermal shocked by the spray quench test. Results of these tests appear in Table XVIII and XIX and in Figures 22 and 23.

Three of the T-joints, J-1, L-2, and L-3 were disqualified because of large fishscaling which occurred when coated with the commercial qualified enamel on the 3/16 inch steel plate. This deficiency developed with the J-1 steel before any quenches were made. On steels L-2 and L-3 the disqualifying defects apparently caused by residual stress from welding were on or near the center of the underside of the 3/16 inch section. In light of results with -S- Enamel, the failure of the T-joints fabricated from steels L-2 and L-3 is believed to be due to the enamel and/or the firing conditions.

The T-joints and all the 4- by 8-inch plates coated by the commercial firm were fired in a production furnace for 15 minutes. As indicated by the enameler's temperature recorder, during the 15 minute firing time the temperature of the furnace varied from 1620° to 1740°F. Some tearing of the coating appeared on all of the T-sections and the T-sections had the appearance of being underfired. Normal firing temperature for this coating was given as 1650°F. The normal maturing range of the same enamel, but low in alumina, is understood to be from 1550° - 1640°F.

Of the 4- by 8-inch plates coated by the commercial enameling firm only six steels passed the thermal quench requirements specified in MIL-P-16961B. Steels H, J-1, L-1, T, N-2 and W-2 all failed because of large chips or fish-scale exposing the basis metal. Steels J-1 and W-2 failed before quenching studies were started. Large chips also occured on the edges of the majority of plates that passed the qualification studies.

Two gallons of the slip used by the commercial enameling firm were obtained and applied by spraying to 4- by 8-inch plates of each of the twelve steels. These plates were fired at 1650°F in a wet atmosphere provided by passing air through water at 25°C. Firing time was 22 minutes for 3/16-inch sections and 27 minutes for 1/4-inch sections. Remaining contract funds did not allow accelerated fishscale or thermal quench studies on these specimens, however, after one week all specimens except J-2, L-2 and L-3 had developed fishscale.

The coating on steel J-1 failed because of large areas of exposed basis metal. The coatings on L-1 and N-1 would have to be classed as marginal because of the depth and size of the fishscale appearing on these specimens. These coatings would have most probably failed in the early quenches from 650°F.

The coatings on steels N-2, T, W-1, W-2 and W-3 all developed very large fishscale which completely covered the plates although none of these fishscale were deep enough to expose bare metal.

4. Photomicrographic Studies of the Enamel-Metal Interface

It can be seen from Tables XIV through XVII that only two steels (J-1 and W-2) failed the accelerated fishscale and thermal quenching tests when coated with -S- Enamel. It will also be noted in Table XVIII that steels J-1 and W-2 were the only steels that fishscaled when coated with the commercial coating before the specimens were thermally quenched. The difference between these two steels and the other steels used in this study is not readily apparent from the heat history or chemical composition of these steels. Photomicrographs of the enamel metal interface were prepared from each steel coated with -S- Enamel in an effort to determine the cause of failure of the coatings on steels J-1 and W-2. These photomicrographs appear in Figures 24 and 25. No apparent cause for the failure of the coatings on steels J-1 and W-2 can be seen either in the enamel or the steel.

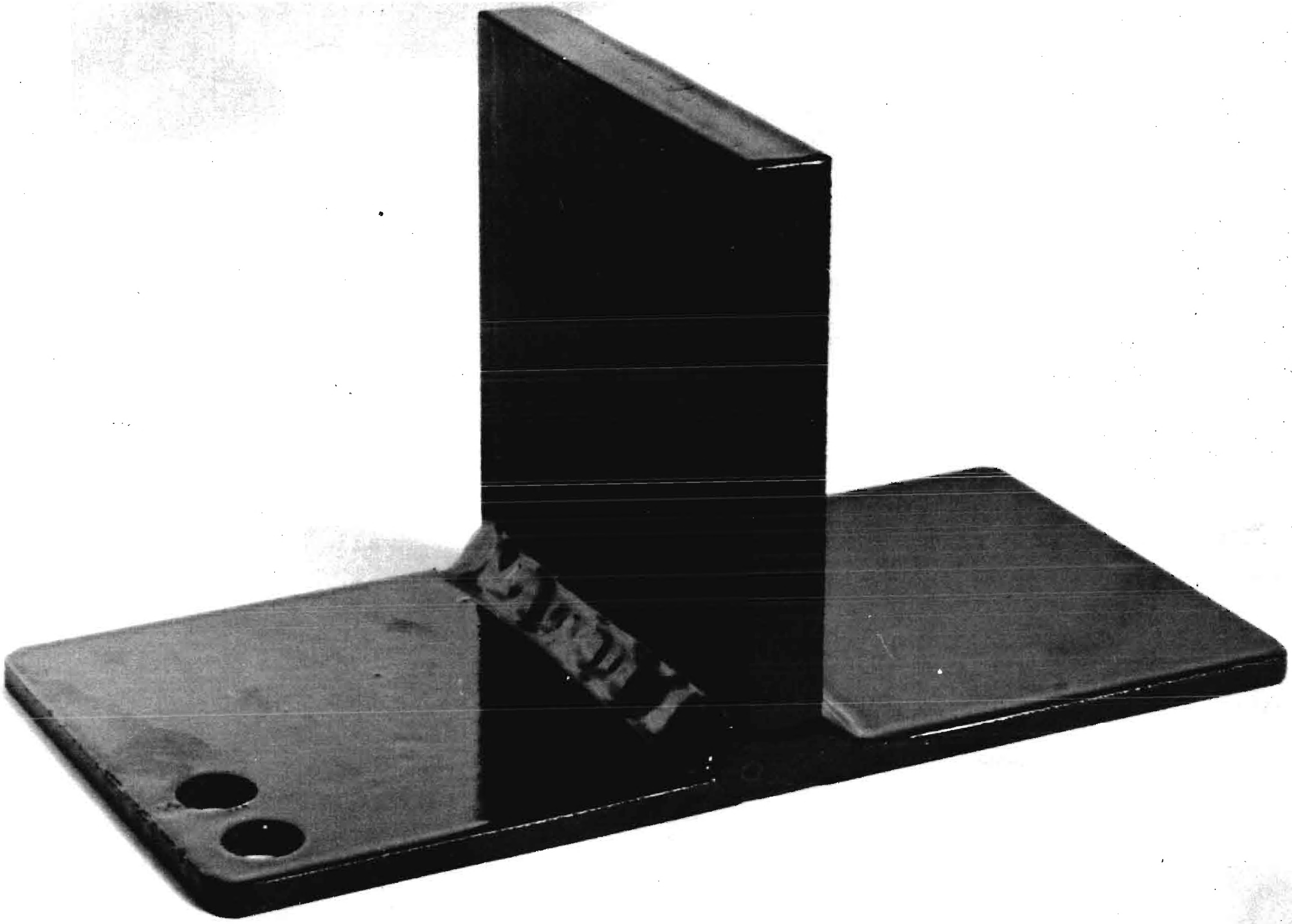


Figure 17. T-Joint Specimen.

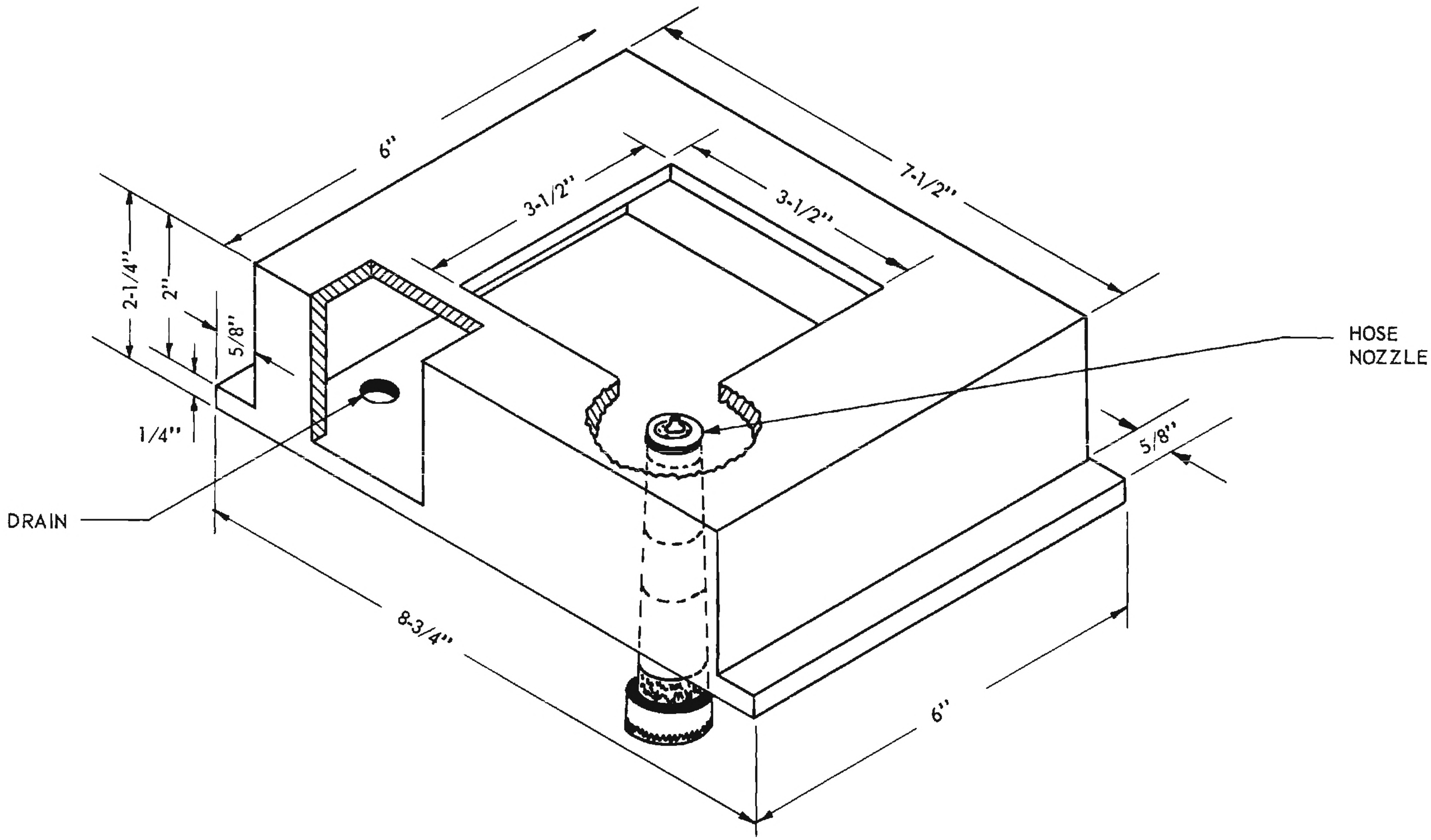


Figure 18. Spray Box for Use in the Spray Quench Test.

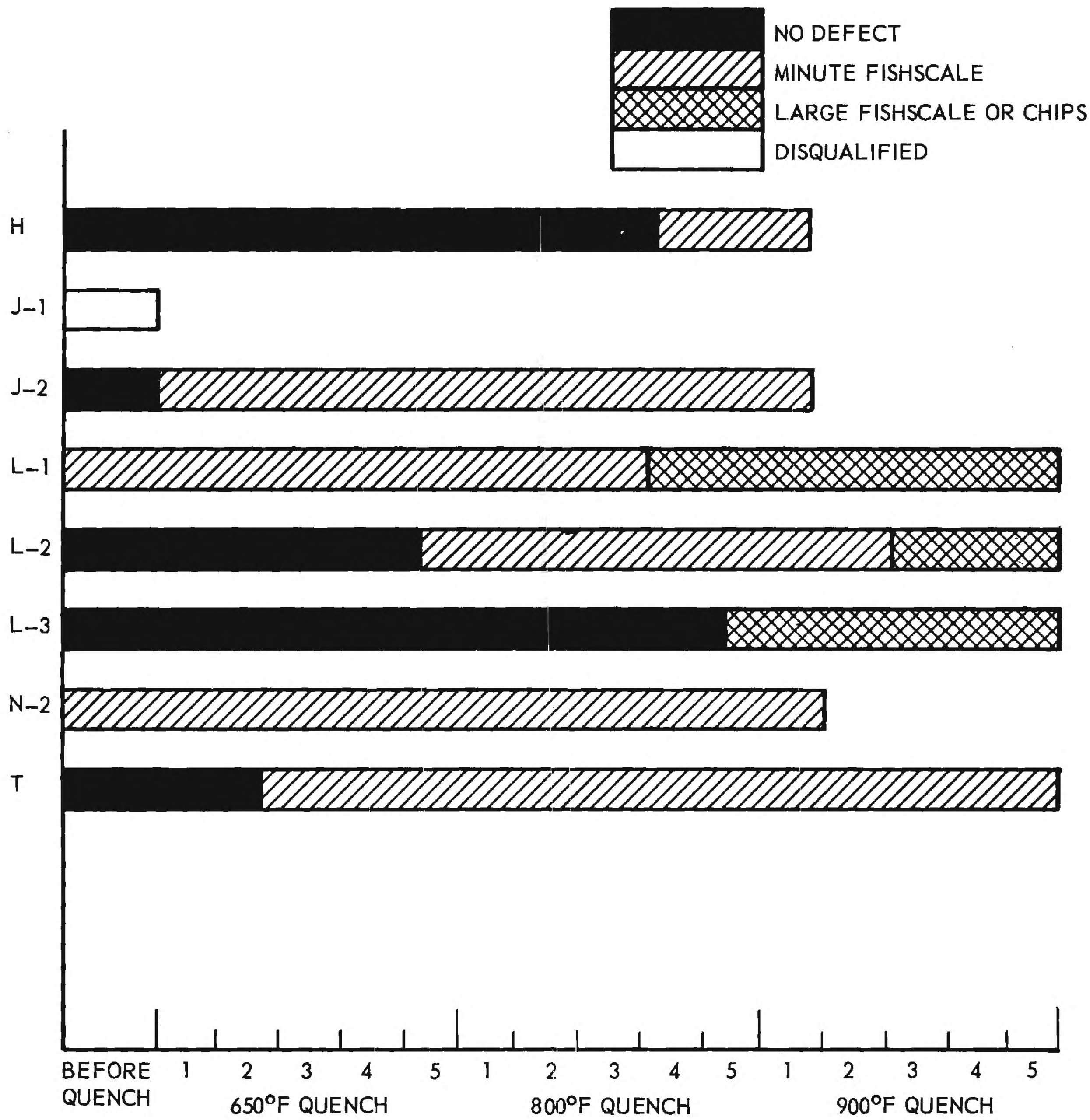


Figure 19. Immersion Quenching of T-Joints Coated with -S- Enamel.

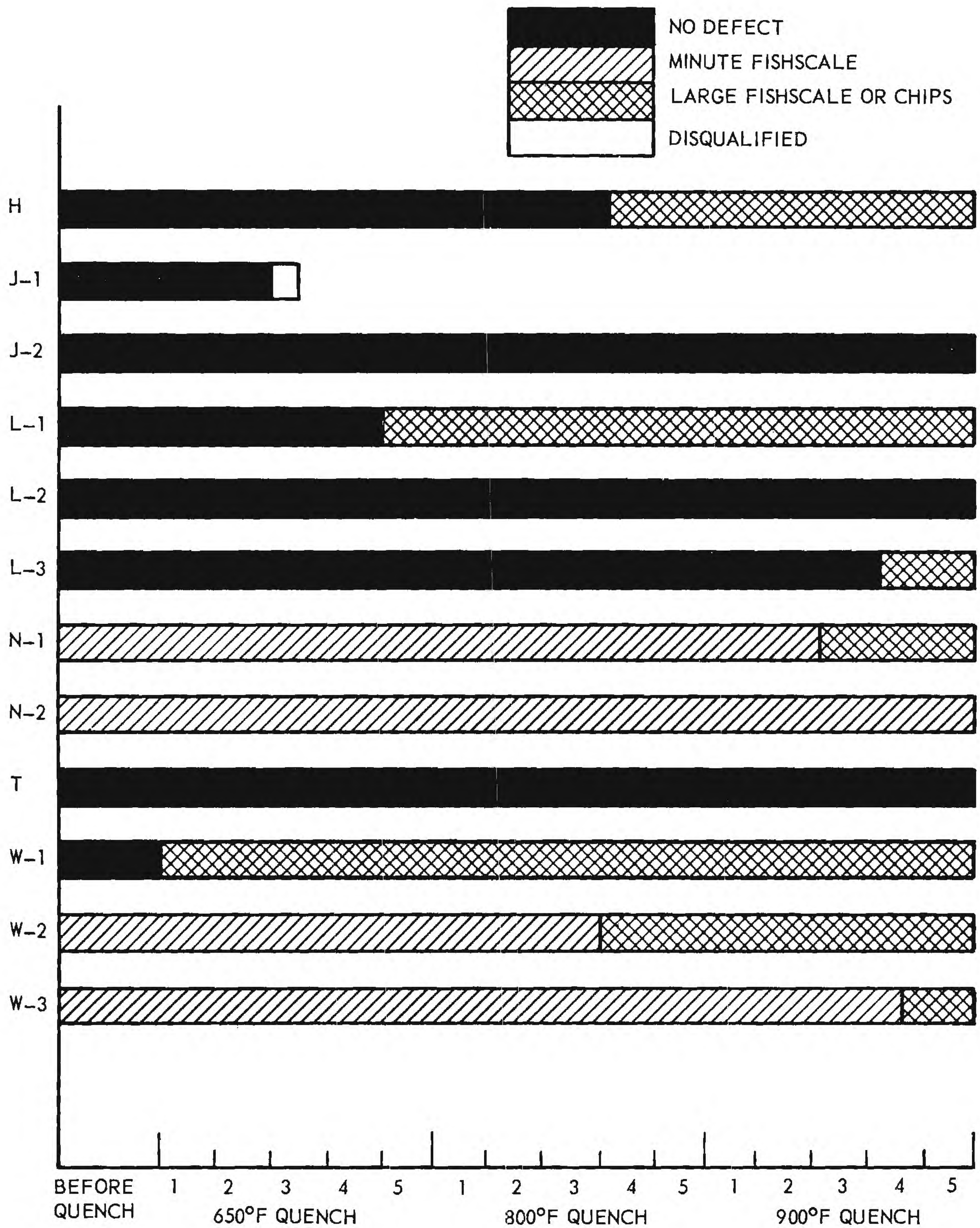


Figure 20. Immersion Quenching of 4- by 8-Inch Plates Coated with -S- Enamel.

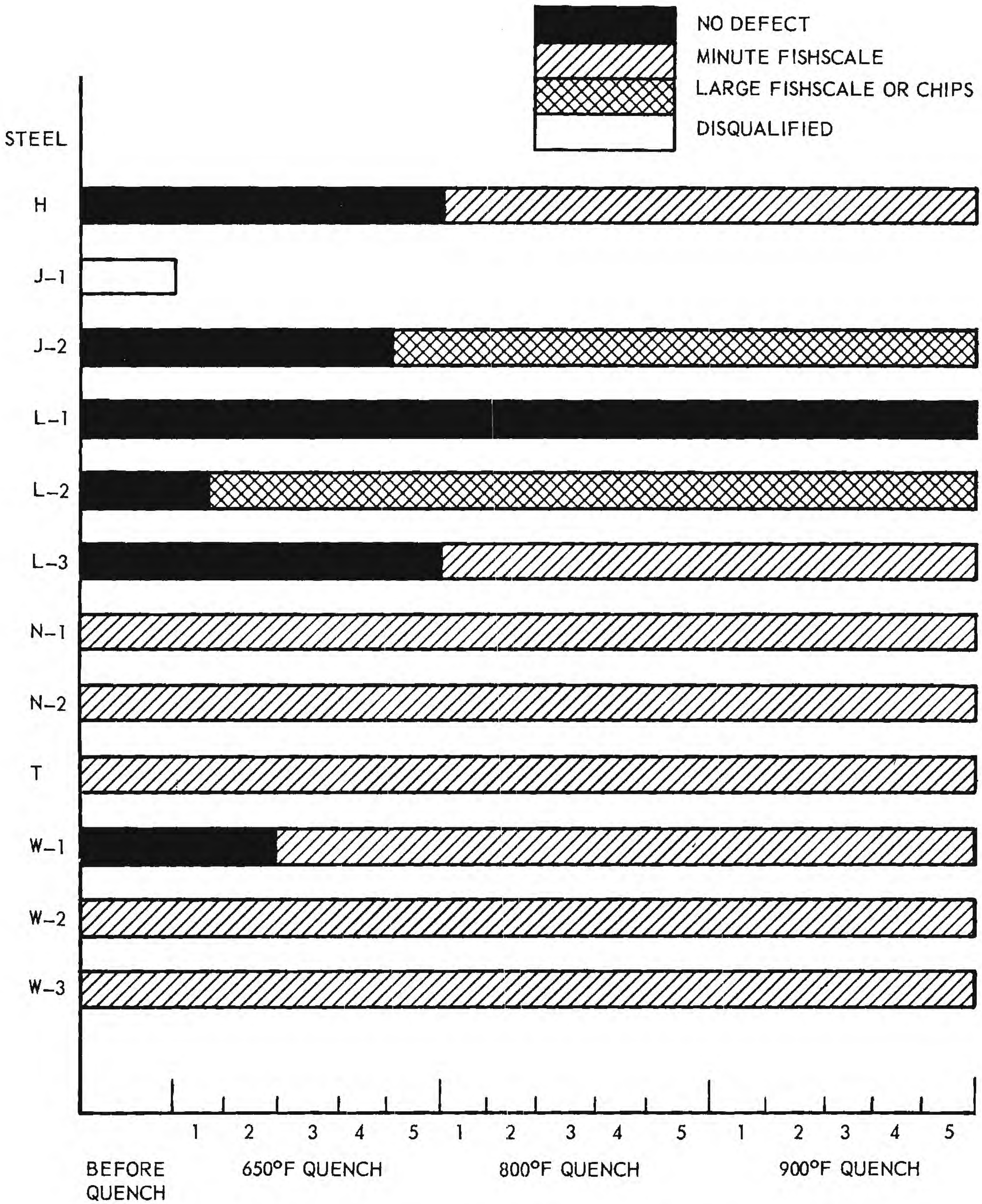


Figure 21. Water Jet Quench Studies of 4- by 8-Inch Plates Coated with -S- Enamel.

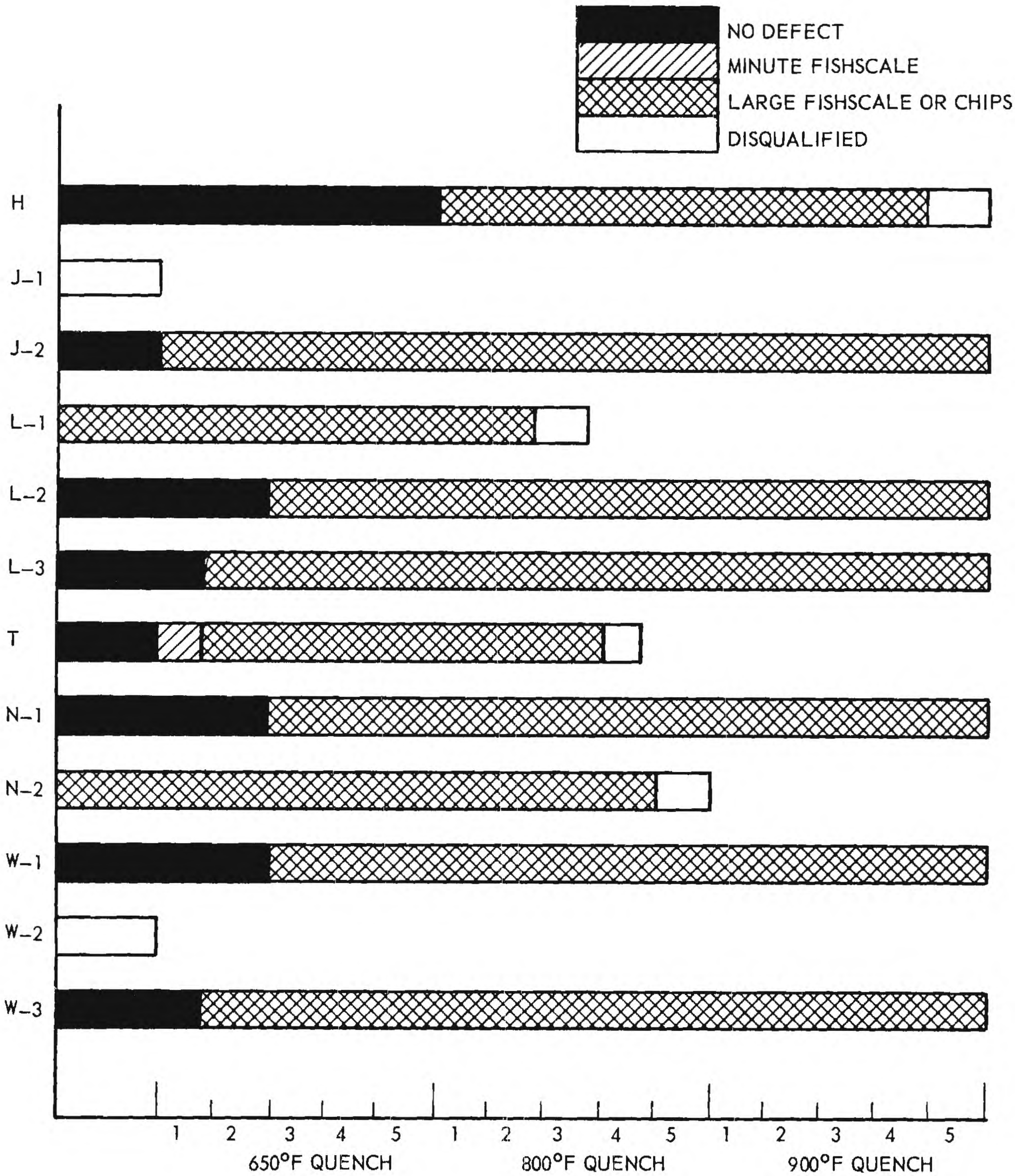


Figure 22. Water Jet Quench Studies of 4- by 8-Inch Plates Coated Commercially.

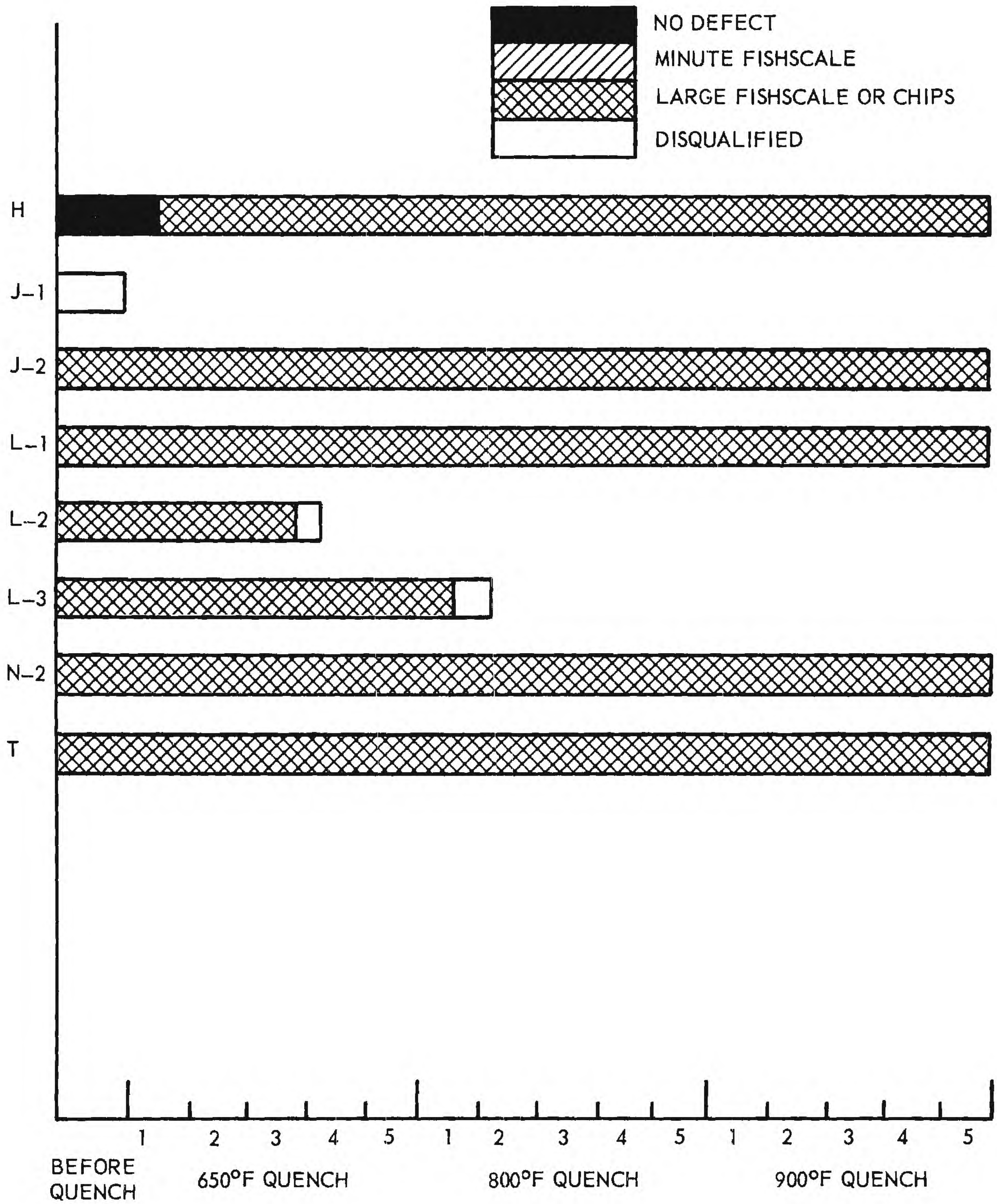
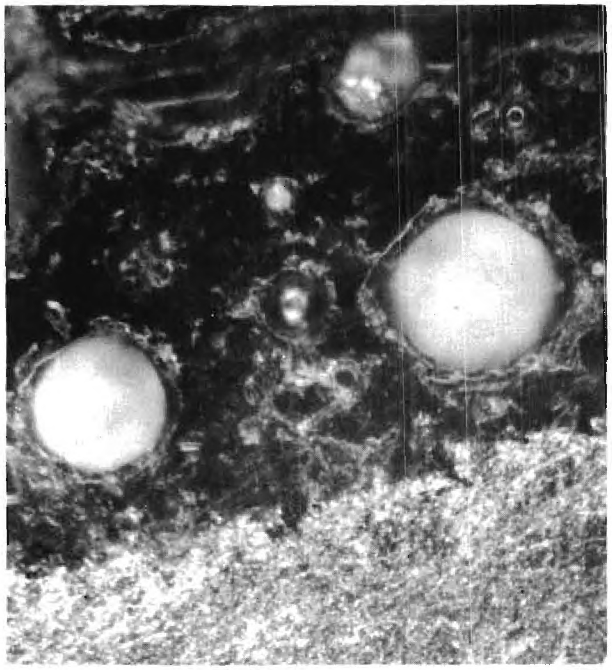
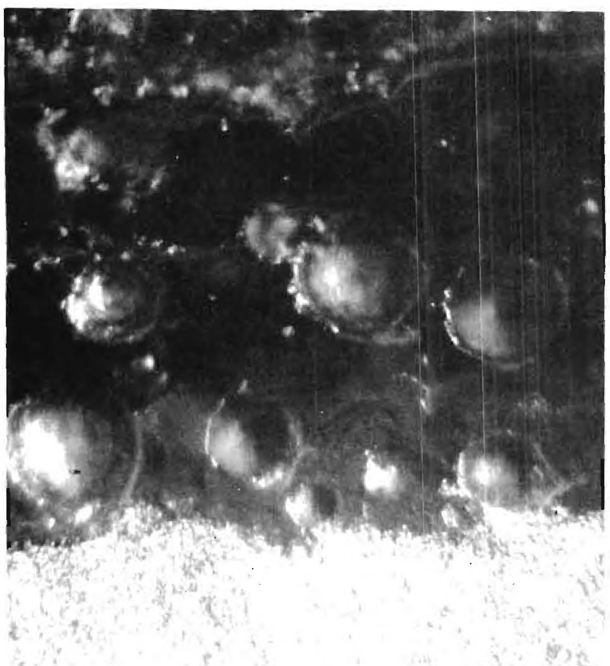


Figure 23. Immersion Quenching of T-Joints Coated Commercially.



(a) H STEEL

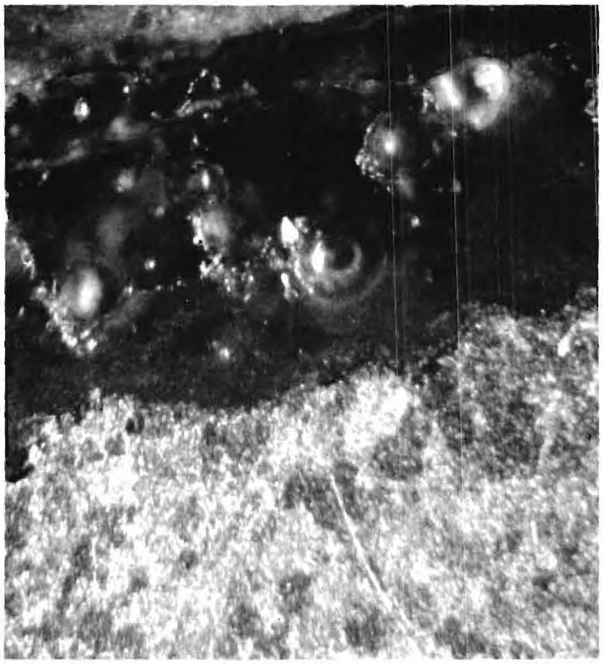
(b) J-1 STEEL



(c) J-2 STEEL

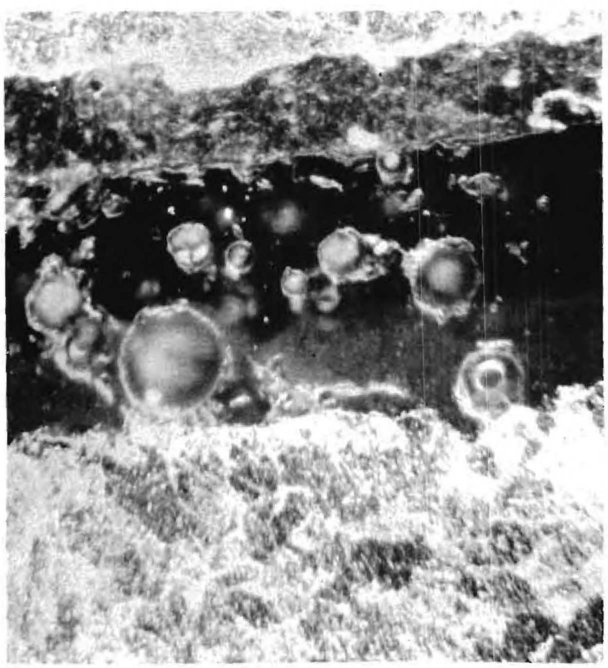
(d) L-1 STEEL

Figure 24. Photomicrographs of Enamel-Metal Interface of Steels Coated with -S- Enamel; Enamel in Focus.



(e) L-2 STEEL

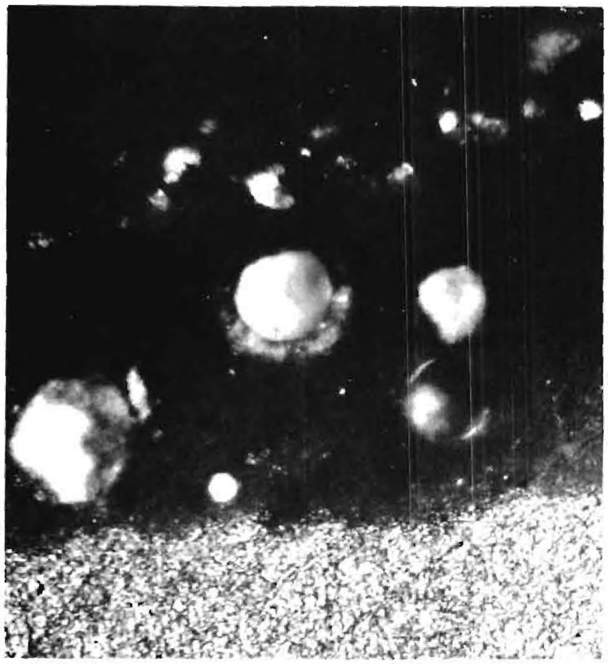
(f) L-3 STEEL



(g) N-1 STEEL

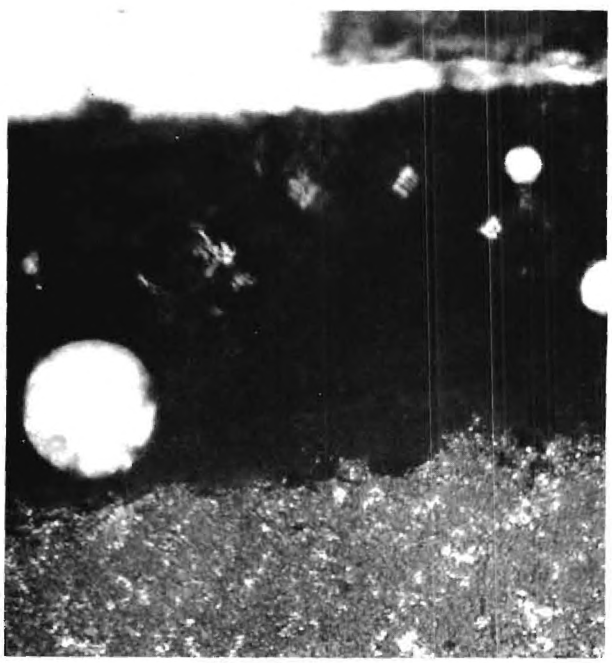
(h) N-2 STEEL

Figure 24 (Continued). Photomicrographs of Enamel-Metal Interface of Steels Coated with -S- Enamel; Enamel in Focus.

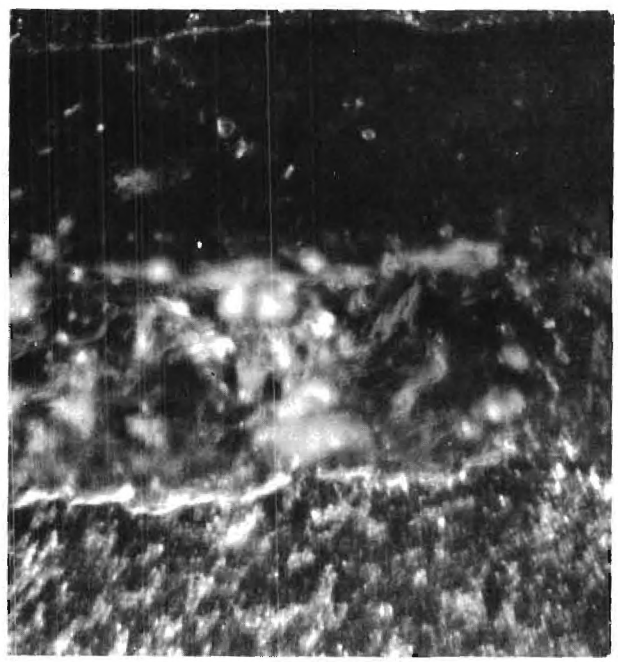


(i) T STEEL

(j) W-1 STEEL

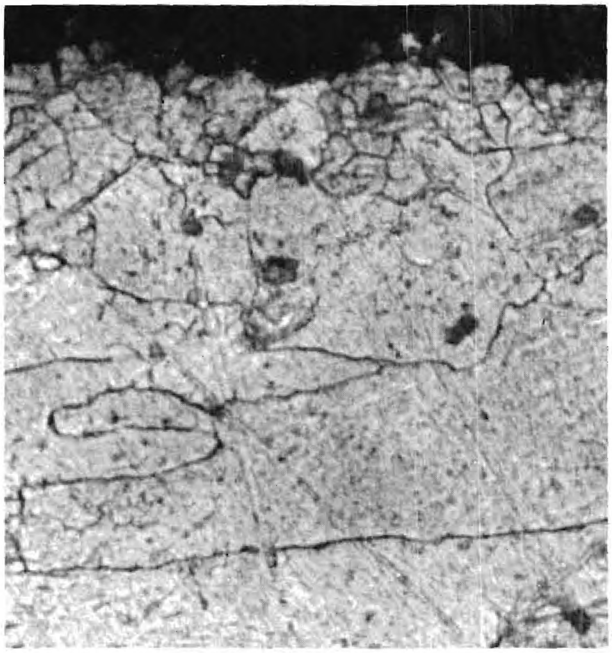


(k) W-2 STEEL

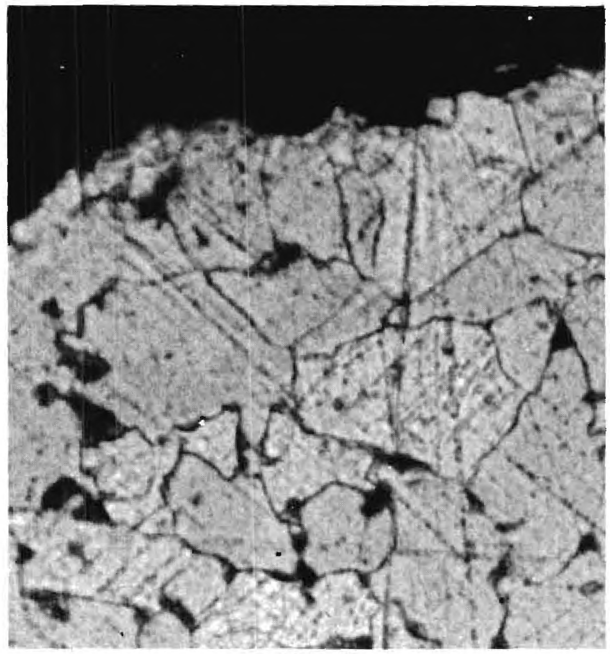


(l) W-3 STEEL

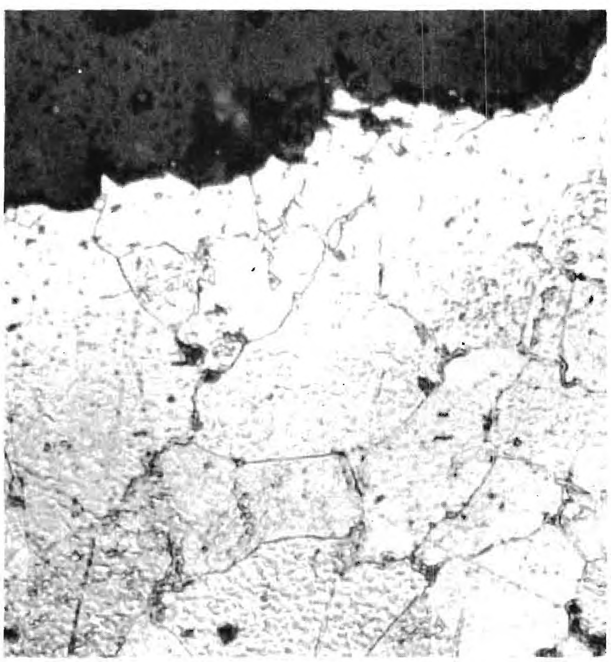
Figure 24 (Continued). Photomicrographs of Enamel-Metal Interface of Steels Coated with -S- Enamel; Enamel in Focus.



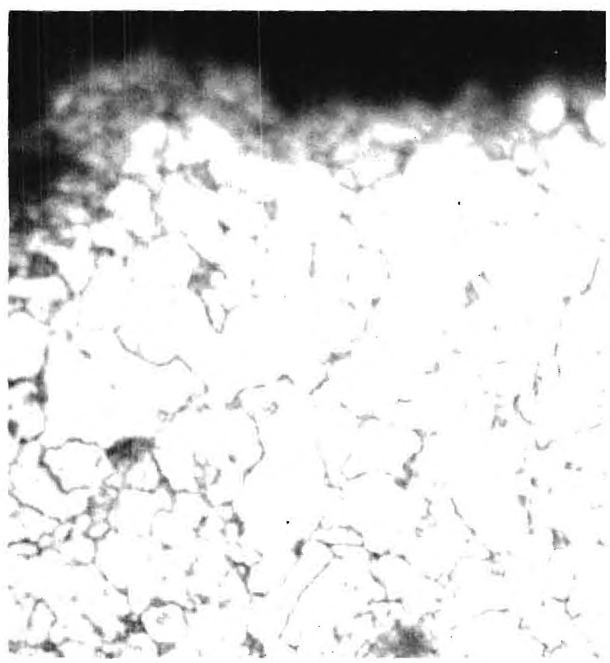
(a) H STEEL



(b) J-1 STEEL

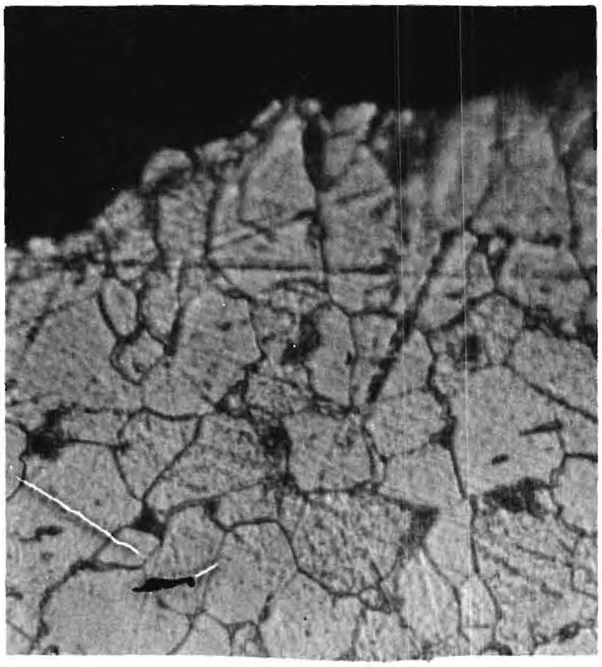


(c) J-2 STEEL

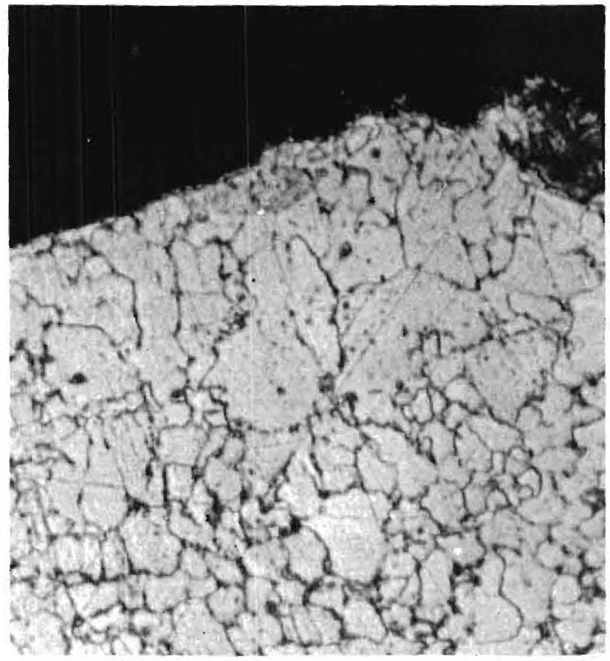


(d) L-1 STEEL

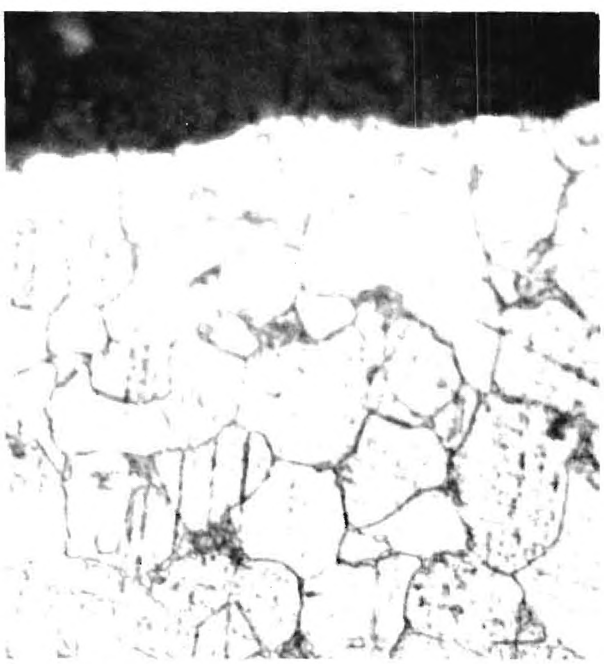
Figure 25. Photomicrographs of Enamel-Metal Interface of Steels Coated with -S- Enamel; Metal in Focus.



(e) L–2 STEEL



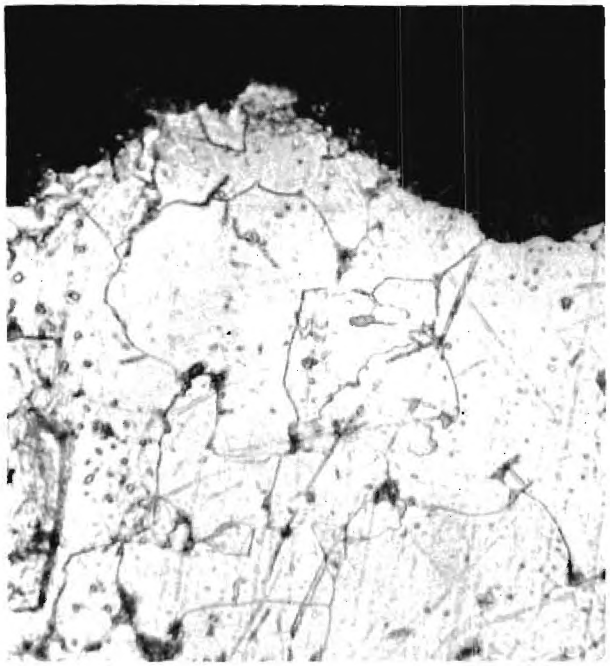
(f) L–3 STEEL



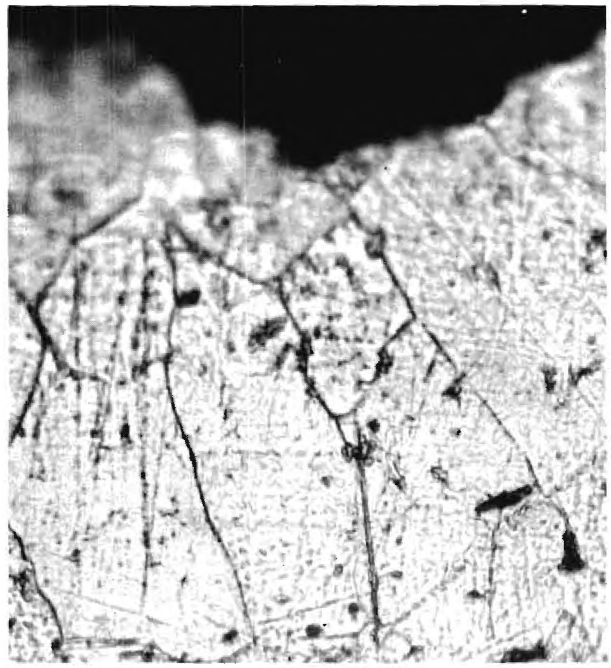
(g) N–1 STEEL

(h) N–2 STEEL

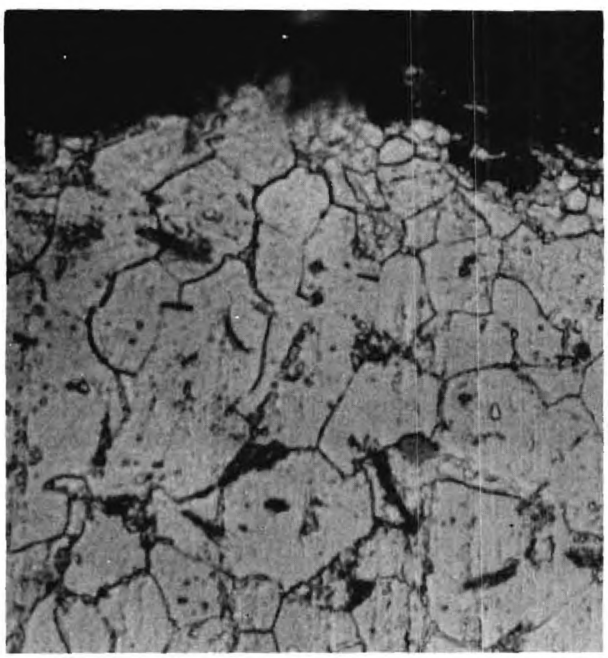
Figure 25 (Continued). Photomicrographs of Enamel-Metal Interface of Steels Coated with -S- Enamel; Metal in Focus.



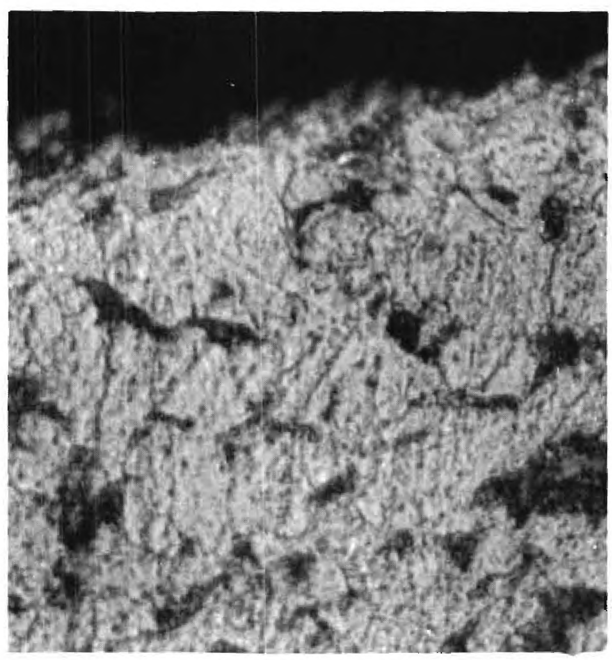
(i) T STEEL



(j) W-1 STEEL



(k) W-2 STEEL



(l) W-3 STEEL

Figure 25 (Continued). Photomicrographs of Enamel-Metal Interface of Steels Coated with -S- Enamel; Metal in Focus.

IV. DISCUSSION

From a technological standpoint, it would be most desirable to arrive at a method of qualifying steel PLATE AND WELDMENTS acceptably receptive to porcelain enameling from some property or combination of properties of the steel alone. It was, therefore, the original objective of this work to study and evaluate such parameters as chemical composition, grain structure, condition of grain boundaries, heat history, method of forming etc. as they might relate to the enamelability of the steel in question.

However, after an extensive study of these properties of steel it was determined that some other factors not so easily discernible presented a greater influence on the enamelability of the steel. It was, therefore, decided that a program would be undertaken to study the feasibility of using a "standard" enamel to qualify the steel in question. This "standard" enamel idealy would be affected by the property or properties of steel which cannot be isolated or studied analytically and reveal its absence or presence and thus provide a means of determining the enamelability of the steel. This would, therefore, provide the basis for qualifying steel PLATE AND WELDMENTS.

The "standard" enamel which resulted from the previous year's work, was selected on the basis that it appeared to have the greatest chance of providing a satisfactory coating on the greatest variety of steels. After evaluating the 12 steels with this enamel it has been found that the coating produced is much less sensitive to the addition of aluminum oxide or the presence of moisture in the furnace atmosphere. It appears, therefore, that nearly ideal properties have been obtained in the "standard" frit as far as thermal shock resistance, fit and adherence are concerned. Thus if defects appear in the coating produced by this frit, it seems unlikely that the addition of alumina or the reduction of moisture in the furnace atmosphere will alleviate the defect. It should, therefore, be safe to say that when defects appear in this coating the cause can be assigned to the steel and not the enamel.

Comparing these results with those obtained when the commercial enamel was applied to the steels under investigation several differences should be noted. (1) The furnace atmosphere is very important, therefore, enameling on "wet" days may well produce defective coatings. (2) The development of bubble film as determined by variations in clay or firing treatment received on thick versus thin steel sections of the component to be enameled may determine the acceptability of the coating. At any rate the "standard" enamel has illustrated the fact that all but two of the steels, even when enameled in a "wet" atmosphere are acceptably receptive to porcelain enameling. Therefore, the commercial enamel would be designated as defective rather than the steel in all but the cases involving the use of J-1 and W-2 steels.

Any of the data obtained with the J-1 and W-2 steel such as chemical composition, heat history, extractable gas, or bubble film would not have suggested that these steels would be of any less an enameling quality than the other steels. Using the commercial enamel for evaluation purposes and firing a "wet" atmosphere might have disqualified at least nine steels. Depending upon the humidity on a particular day it might have disqualified any number from these nine to only J-1 and W-2. However, the selected "standard" enamel only disqualified the J-1 and W-2 even in a "wet" atmosphere proving that all but these two steels could be successfully porcelain enameled regardless of the humidity if a suitable enamel was used.

When steels J-1 and W-2 were coated with the standard enamel and fired in an atmosphere containing only atmospheric moisture no defects were noted as a result of the accelerated fishscale test or the immersion quench test. Therefore, it would be assumed that using the "standard" enamel represents an almost universal enamel which may provide satisfactory coatings on almost any steel if applied in an atmosphere containing a minimum of moisture.

This situation points out the fact that enameled steel should be considered as a composite system and emphasizes the difficulty in considering porcelain enamel and steel independently. Thus a given steel may provide an excellent substrate for one enamel and be poison for another. In other words it may be possible to develop or find an enamel which will provide a satisfactory coating on the poorest steel as determined by its inability to be satisfactorily coated by other enamels. Thus as far as this one enamel is concerned the steel is qualified.

It should be the aim of this work however to provide a "standard" enamel which will represent some intermediate in its ability to produce a satisfactory coating on a large number of steels. Thus, although the "standard" used in this program provides a satisfactory coating for all steels when fired in a dry atmosphere, it failed on two steels when fired in a wet atmosphere. It would thus be marginal to defective on the J-1 and W-2 steels depending upon the degree of moisture present in the firing atmosphere. Therefore, it would seem appropriate to qualify each steel by firing the "standard" enamel in a wet atmosphere.

It should be reemphasized that the commercial enamel being used for the porcelain enameling of steel plate for shipboard use is at best marginal. Firing in a wet atmosphere would probably provide defective coatings on a large majority of steels selected. Firing under ideal or at least low moisture conditions disqualified this coating system using half of the steels investigated. Therefore, it would not be surprising to find this enamel producing defective coatings in many cases.

It may, therefore, be an additional objective of the qualifying test using the "standard" coating not only to qualify the steel in question, but also to evaluate the enamel being used by the enameling firm for whom the steel is qualified. Thus by using the commercial enamel to coat qualified steel under dry and "wet" firing conditions some indication may be derived as to the susceptability of the enamel to atmospheric moisture induced defects.

A. Standard Qualifying Frits

Although the art of frit smelting is old, the attainment and control of specific frit properties is not an easy task. The recent development of low temperature frits represents a significant advancement in porcelain enamel technology. Hence, chemical formulation alone may not be sufficient to define the properties of the frit. This is to say, for example, that a difference may well exist between two different frits depending upon whether the soda was provided from sodium silicofluoride, sodium nitrate or sodium carbonate, all other things being equal. The state of oxidation of each constituent, and thus its role in the frit depends upon the proportion of oxygen provided by the raw batch, the smelting time, and combustion atmosphere. If smelting time and temperature are not held constant, volatile fluxes such as fluorides will be decomposed and the liberated fluorine driven from the batch, resulting in a final product with a higher melting point than intended. An example of this can be seen in Table VII. The wide range in per cent fluorine was obtained even though firing time and temperature were held as constant as possible under existing laboratory conditions.

Assuming that the desired frit can be achieved, the problem arises as to whether each facility which smelts the prescribed "reagent" batch will have identical smelting conditions.

It is not considered impossible that sufficient control could be exercised over the smelting operation to produce identical frits. However, it is felt that the instrumentation, equipment and calibration of such a system would be prohibitively expensive. Such instrumentation as would provide analysis of gas evolved during smelting to control the process would undoubtedly be required. Methods of agitation with a controlled atmosphere would have to be developed. Generally, the entire study would be of an analytical nature in an area of glass technology which is essentially unexplored.

An alternate choice would appear to be the acquisition of a large quantity, perhaps two or more tons, of a "reagent" frit from a frit manufacturer. This frit could then be used for the qualification of steels. Certain steels could be set aside as reference samples. At some later date when a new supply of "reagent" frit is required these reference steels could be used to "calibrate" a new supply of frit. At this time it is considered desirable to purchase the "reagent" frits from a commercial source, since this would provide a large quantity of frit which would be consistent throughout, thus eliminating any lack of reproducibility between facilities attempting to smelt the same formulation. Although a second supply of frit may differ from the first, a correlation between the two supplies of frit should be possible.

B. "Reagent" Clay

The use of Differential Thermal Analysis and a "proof test" consisting of observation of the bubble stratum of a porcelain enamel containing the clay under investigation, would seem to be sufficient to select a clay for use in a "standard qualifying" or "reagent" porcelain enamel slip. Results of the studies carried out on eight clays did not indicate that clays containing the largest amounts of chemically combined water produce the best bubble strata; however, these clays did produce enamel coatings with fewer gaseous defects. It would seem that this greater amount of water released just below enameling temperatures (610°C) would be detrimental to the enamel coating due to the reaction of iron and water at enameling temperatures (746°C) injecting large amounts of hydrogen into the steel. It would be thought that greater amounts of gas effusing from the metal at room temperature would cause more defects in the coating. This does not seem to be the case in that enamel coatings made with clays containing the largest amounts of chemically combined water produce enamel coatings with fewer gaseous defects. This might be attributed to the fact that the clays containing large amounts of chemical water help form large evenly spaced bubbles in the bubble stratum that help relieve stresses in the glass. Moore, Pitts and Harrison* have suggested that bubbles at the enamel-iron interface evidently serve as reservoirs for the hydrogen which diffuses from the steel structure after the specimen has cooled.

C. Gas Extraction Crucible Test

It is not recommended that the crucible test be adopted at this time for a standard gas extraction test. A greater quantity of frit and a greater length of time is necessary for preparing samples than when coating gas

*D. G. Moore, J. W. Pitts, and W. N. Harrison, Role of Nickel Dip in Enameling of Sheet Steel, J. Am. Ceram. Soc. 37, 363-69 (1954) extraction specimens with a normal porcelain enamel slip. Also the crucible test is only a method of producing gas in the steel and does not in any way duplicate coating and firing conditions that would be encountered in enameling steel plate. Therefore, the value of this test in qualifying steel plate is doubtful. If the crucible test should be considered, other controlling factors must be evaluated before such a test could be standardized.

D. Qualification of Steel Plate

1. Gas Extraction

At the beginning of this study it was thought that it might be possible to use gas extraction as a procedure for qualifying steel plate acceptably receptive to porcelain enamel coatings by establishing a maximum allowable amount of extractable gas. Of the twelve steels employed in this study, only two failed when coated with -S- enamel. It can be seen from Table XII and Figure 15 that steels J-1 and W-2 which failed had an average amount of gas which fell in the middle of the range of the 12 steels tested. Attempts were made to obtain a correlation between the amount of gas extracted and the chemical composition and heat history of each steel, however, this was not successful. The erratic values obtained with some of the steels might be traced to the fact that gas extraction samples were cut randomly from each steel plate and were not taken from any one area of the plate. Gas extraction studies under the previous contract had been made with specimens cut from adjacent areas of the plate. Differences in rolling or surface treatments over the entire area of the plate may have accounted for the wide differences in gas extraction values obtained with some of the steels. It should be noted, however, that no gas was extracted from steel -H- when coated with either -S- Enamel or with -S- Enamel containing 10 per cent fused alumina. Steel -H- is a low carbon, pickled, commercial, enameling quality "sheet". This steel showed no disqualifying defects and had fewer minute fishscale surface defects than any of the steels studied.

The two steels that did not pass the thermal quench and adherence tests (J-1 and W-2) had more than 0.30 ml of gas extracted from the 1 1/2 x 2-inch specimens. However, two specimens (J-2 and L-1) had more than 0.30 ml of gas extracted and still passed qualification test of MIL-P-16961B. Gas extraction values for steel J-2 were erratic and this could be responsible for the high average value, however, steel L-1 had high values in all cases. The near failure or marginal condition of the commercial coating fired in a wet atmosphere on steel L-1 might have a causative relationship to this high extractable gas content.

Gas extraction values obtained from specimens which were coated with standard enamel containing fused alumina did not show any definite relationship between gas extracted and tendency to fishscale, nor did these values show any relationship to those obtained from the alumina free enamel. Therefore, the hypothesis below which was advanced from the results of the previous contract does not hold true.

(1) Addition of a particular type of alumina to certain mill batches of slip, including a particular frit and a particular clay, caused an increase in the extractable gas content of certain steel plates to which the slip was applied and fired under specific conditions, (2) when other steel plates were enameled with the same mill batches, the alumina addition caused a decrease in extractable gas content, and (3) when the same steel plates were coated with enamel conforming to MIL-P-16961B, those exhibiting an

increase in extractable gas were associated with the formation of fishscales in the coating, and those exhibiting a decrease in extractable gas were not associated with the formation of fishscales.

Since the above hypothesis does not appear true, the only value of the gas extraction test would seem to be the possibility of setting a maximum allowable amount of gas to be extracted from a 1 1/2- x 2- x 3/16-inch steel specimen which had been coated with the "standard qualifying enamel". From the results of the study in Table XII the best value would appear to be 0.30 ml. This value would eliminate steels J-2 and L-2 which passed the other qualification tests, however, these steels could still be qualified under Case II listed in Section D of the experimental work.

2. Accelerated Fishscale Studies

The accelerated fishscale studies proved of value in determining gaseous defects in enameled specimens. Steel J-1 failed immediately upon cooling, however, steel W-2 did not fail when coated with -S- Enamel until accelerated fishscale studies were carried out at 225°C. All other steels were found suitable for the qualification test requirements of MIL-P-16961B. Of the specimens coated by the commercial enameling firm, none of the coatings failed upon cooling to room temperature; however, the coatings on J-1 and W-2 failed before they were returned to the contractor's laboratory.

All but three of the steel specimens coated with the commercial enamel and fired in the "wet" atmosphere developed large fishscale upon cooling. Based on the results obtained with the "standard" enamel, this fishscaling would be attributed to the enamel in all cases except for the J-1 and W-2 steel. Steel J-1 was disqualified due to exposed metal. Steel W-2 would have probably failed in the early quenches from 650°F as would have the other steels showing large amounts of fishscale.

The accelerated fishscale test provides a quick method for indicating whether or not a steel plate would be expected to fail when coated with porcelain enamel. The thermal quench study did not indicate failure of coating on W-2 steel in the same manner as the accelerated fishscale study. Therefore, the accelerated fishscale test appears essential to complete specification for enameling quality steel.

3. Spalling (Thermal Quench)

All steels with the exception of J-1 passed the spalling test both by immersion and by the water-jet quench method. There appears to be very little difference between the water-jet quench and the immersion quench technique. After completing all three quench cycles results are very similar.

4. Correlation of Enameling Studies

Six steel specimens coated by the commercial enameling firm failed to pass the thermal shock qualification test of MIL-P-16961B (Figure 22). Only two steels did not pass this qualification and the accelerated fishscale studies when coated with -S- Enamel fired under high humidity conditions. All steels failed when they were coated with the commercial enamel in the contractor's laboratory and fired under high humidity conditions used with the "standard qualifying enamel". This work shows the cause of failure of the commercial coating on steels H, L-1, N-2 and T not necessarily to be in the steels but possibly lies in the commercial enamel coating applied to these steels or in the method of application. The cause of failure of coatings on steels J-1 and W-2 can be placed with the steels since these two steels failed when coated with both enamel systems, therefore it is believed that coating of sample steel specimens with a "standard qualifying enamel" can be used as the basis for a qualification test of enameling quality steel plate.

V. CONCLUSIONS

From the results of this work it appears that steel plate for enameling purposes can best be qualified by the use of a "standard qualifying" porcelain enamel coating. This coating should include a commercial frit or frits which can produce an enamel coating capable of passing the T-joint quench test requirements of MIL-P-16961B and an accelerated fishscaling test. These frits should be purchased in large quantities and kept on hand in Government laboratories thus minimizing chance of variation in the composition and performance of the frit; such as might occur if these frits were purchased in small quantities over a period of time or laboratory batch smelting attempted. Several steel plates with known enameling characteristics could be kept on hand to be used to "calibrate" a new frit supply once the original supply was expended.

A well crystallized enameling clay containing a large quantity of chemically combined water should be used. This can be selected on the basis of differential thermal analysis, in addition to parameters commonly specified for enameling clay.

After the plate being studied for qualification is coated, any delayed gaseous defects can be made to appear much quicker by heating the plate to 175°F for 24 hours then to 225°C for an additional 24 hours. The use of this test is essential since the same defects do not always show up in quenches on T-joints and 4- by 8-inch plates subjected to thermal shock.

The T-joint specimen used in qualifying porcelain enamel coatings under MIL-P-16961B should be used for qualifying steel plate especially when welding of the final product for which the steel is intended is necessary. Any. strains induced in the metal by welding which might cause failure of the enamel coating will be shown by the enameled T-joint specimens. Also, if the steel is of marginal quality differences in heating on thick and thin sections keeping the enameling operation from being ideal may cause failure of the coating.

The use of the gas extraction test appears questionable since the cause for variation in amount of gas extracted from some types of specimens appears unexplainable. If the gas extraction test is used as a part of the qualification of steel plate, then the maximum allowable extractable gas for 1-1/2- x 2- x 3/16-inch steel specimens would have to be set at 0.30 mil, and the standard enamel coating matured in a "wet" atmosphere.

Steel plate can be qualified by use of a "standard qualifying enamel", subjecting coated specimens to the accelerated fishscale test and to the thermal quench cycles outlined in MIL-P-16961B. The following criteria would apply:

Case I - Extractable gas, satisfactory (low)
Accelerated fishscale, Negative (No fishscale)
Spalling, None
Material acceptable

Case II - Extractable gas, excessive
Accelerated fishscale, negative (No fishscale)
Spalling, None
Of questionable acceptance because high extractable gas, no spalling tendency might be cause for negative fishscale result; gas could have been sealed in by enamel. In this case the accelerated fishscale test on the quenched spalling test specimens would be re-run. If the accelerated fishscale remains negative the steel plate would be acceptable.

Case III - Extractable gas, satisfactory

Accelerated fishscale, positive

No need to run spalling; plate rejected.

Case IV - Extractable gas, satisfactory

Accelerated fishscale, negative

Spalling, positive

Material would be unacceptable because steel is insufficiently reactive to bond well with the enamel.

Respectfully submitted:

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Approved:

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VI. APPENDIX

TABLE XV

IMMERSION QUENCH OF T-JOINTS
COATED WITH -S- ENAMEL

T-Joint	Before Quench
H	No Defect
J-1	Fishscale (bare metal exposed)
J-2	No Defect
L-1	Minute Fishscale $4/cm^2$
L-2	No Defect
L-3	No Defect
N-2	Minute Fishscale $3/cm^2$
T	No Defect

T-Joint	650°F Quench Cycles				
	1	2	3	4	5
H	No Change	No Change	No Change	No Change	No Change
J-2	Minute Fish-scale $4/cm^2$	Minute Fish-scale $6/cm^2$	No Change	No Change	No Change
L-1	No Change	No Change	No Change	No Change	No Change
L-2	No Change	No Change	No Change	No Change	Minute Fish-scale $5/cm^2$
L-3	No Change	No Change	No Change	No Change	No Change
N-2	Minute Fish-scale $5/cm^2$	No Change	No Change	No Change	No Change
T	No Change	Minute Fish-scale $3/cm^2$	No Change	No Change	No Change

TABLE XV (Continued)

IMMERSION QUENCH OF T-JOINTS
COATED WITH -S- ENAMEL

T-Joint	800°F Quench Cycles				
	1	2	3	4	5
H	No Change	No Change	Minute Fish-scale 2/cm^2	No Change	No Change
J-2	No Change	No Change	No Change	No Change	No Change
L-1	No Change	No Change	Edge Chip 1/8 inch	No Change	Edge Chip 1/8 inch
L-2	No Change	No Change	No Change	No Change	No Change
L-3	No Change	No Change	No Change	No Change	Edge Chip 1/8 inch
N-2	No Change	No Change	No Change	No Change	No Change
T	No Change	No Change	No Change	No Change	No Change

T-Joint	900°F Quench Cycles				
	1	2	3	4	5
H	Minute Fish-scale 3/cm^2	-	-	-	-
J-2	No Change	-	-	-	-
L-1	Chip 1/8 inch	Minute Fish-scale 5/cm^2	No Change	No Change	No Change
L-2	No Change	Edge Chip 1/8 inch	No Change	No Change	No Change
L-3	No Change	Edge Chip 1/8 inch	Minute Fish-scale 3/cm^2	Minute Fish-scale 5/cm^2	No Change
N-2	No Change	-	-	-	-
T	No Change	Minute Fish-scale 4/cm^2	No Change	No Change	No Change

*Disqualifying Defect

TABLE XVI

IMMERSION QUENCH OF 4- by 8- INCH PLATES
COATED WITH -S- ENAMEL

Plate Type	Average Coating Thickness (Mils)	Before Quenching
H	6.0	No Defect
J-1	6.7	No Defect
J-2	8.6	No Defect
L-1	6.2	No Defect
L-2	6.7	No Defect
L-3	8.0	No Defect
N-1	9.5	Minute fishscale 6/cm^2
N-2	6.0	Minute fishscale 5/cm^2
T	6.3	No Defect
W-1	4.5	No Defect
W-2	10.0	Minute fishscale 4/cm^2
W-3	9.0	Minute fishscale 3/cm^2

TABLE XVI (Continued)

IMMERSION QUENCH OF 4- by 8- INCH PLATES
COATED WITH -S- ENAMEL

Plate Type	650°F Quench Cycles				
	1	2	3	4	5
H	No Change	No Change	No Change	No Change	No Change
J-1	No Change	3/16 fish-scale (1) to bare metal	No Change	No Change	No Change
J-2	No Change	No Change	No Change	No Change	No Change
L-1	No Change	No Change	No Change	1/16 edge chips (2)	No Change
L-2	No Change	No Change	No Change	No Change	No Change
L-3	No Change	No Change	No Change	No Change	No Change
N-1	No Change	No Change	No Change	No Change	No Change
N-2	No Change	Minute fish-scale 10/cm^2	Minute fish-scale 13/cm^2	No Change	No Change
T	No Change	No Change	No Change	No Change	No Change
W-1	1/16 fish-scale (2)	No Change	No Change	No Change	No Change
W-2	No Change	No Change	No Change	No Change	No Change
W-3	No Change	No Change	No Change	No Change	No Change

TABLE XVI (Continued)

IMMERSION QUENCH OF 4- by 8- INCH PLATES
COATED WITH -S- ENAMEL

Plate Type	800°F Quench Cycles				
	1	2	3	4	5
H	No Change	No Change	1/16-edge chip	No Change	No Change
J-1	No Change	No Change	No Change	No Change	No Change
J-2	No Change	No Change	No Change	No Change	No Change
L-1	No Change	No Change	No Change	No Change	No Change
L-2	No Change	No Change	No Change	No Change	No Change
L-3	No Change	No Change	No Change	No Change	No Change
N-1	No Change	No Change	No Change	No Change	No Change
N-2	No Change	No Change	No Change	No Change	No Change
T	No Change	No Change	No Change	No Change	No Change
W-1	No Change	No Change	No Change	1/8" fish-scale	No Change
W-2	No Change	No Change	Edge Chip	No Change	No Change
W-3	No Change	No Change	No Change	No Change	No Change

TABLE XVI (Continued)

IMMERSION QUENCH OF 4- by 8- INCH PLATES
COATED WITH -S- ENAMEL

Plate Type	900°F Quench Cycles				
	1	2	3	4	5
H	No Change	No Change	No Change	No Change	No Change
J-1	1/8" fish-scale (1)	3/16" fish-scales (2)	1/8 edge chip (6)	No Change	No Change
J-2	No Change	No Change	No Change	No Change	No Change
L-1	1/16 edge chip (1)	No Change	No Change	No Change	No Change
L-2	No Change	No Change	No Change	No Change	No Change
L-3	No Change	No Change	No Change	1/16 edge chip (1)	No Change
N-1	No Change	No Change	1/16 edge chips (2)	No Change	No Change
N-2	No Change	No Change	No Change	No Change	No Change
T	No Change	No Change	No Change	No Change	No Change
W-1	1/8" fish-scales (2)	No Change	No Change	No Change	No Change
W-2	No Change	No Change	No Change	No Change	No Change
W-3	No Change	No Change	No Change	1/16 edge chips (4)	No Change

TABLE XVII

WATER JET QUENCH OF 4- X 8- INCH PLATES
COATED WITH -S- ENAMEL

Type of Steel	BEFORE QUENCH	Coating Thickness
H	No Defect	8.7
J-1	3/16 inch fishscale (failed exposed metal)	6.25
J-2	No Defect	9.7
L-1	No Defect	6.7
L-2	No Defect	8.3
L-3	No Defect	8.5
T	Minute fishscale 6/cm^2	4.5
N-1	Minute fishscale 20/cm^2	5.3
N-2	Minute fishscale 6/cm^2	5.3
W-1	No Defect	9.5
W-2	Minute fishscale 8/cm^2	8.5
W-3	Minute fishscale 10/cm^2	7.5

Type of Steel	650^{o}F Quench Cycles				
	1	2	3	4	5
H	No Change	No Change	No Change	Sandy	No Change
J-2	No Change	No Change	No Change	No Change	Fishscale 1/8"
L-1	No Change	No Change	No Change	No Change	Sandy
L-2	No Change	Fishscale 1/16"	No Change	No Change	No Change
L-3	No Change	No Change	No Change	No Change	No Change
T	Minute fish-scale 6/cm^2	No Change	No Change	Minute fish-scale 8/cm^2	No Change

TABLE XVII (Continued)

WATER JET QUENCH OF 4- X 8- INCH PLATES
COATED WITH -S- ENAMEL

Type of Steel	650°C Quench Cycles				
	1	2	3	4	5
N-1	Minute fish-scale 20/cm^2	No Change	No Change	No Change	No Change
N-2	Minute Fish-scale 6/cm^2	No Change	No Change	Minute Fish-scale 8/cm^2	No Change
W-1	No Change	No Change	Minute Fish-scale 3/cm^2	No Change	No Change
W-2	No Change	Minute Fish-scale 12/cm^2	Minute Fish-scale 16/cm^2	No Change	No Change
W-3	No Change	No Change	Minute Fish-scale 14/cm^2	No Change	No Change
Type of Steel	**800°F Quench Cycles**				
H	Sandy & Minute Fishscale 4/cm^2	Increased Sandiness	Minute fish-scale 6/cm^2	No Change	No Change
J-2	Chip on edge 1/16	Increase edge chipping	No Change	No Change	No Change
L-1	No Change	No Change	No Change	No Change	No Change
L-2	Chips on edge 1/16	Increased chipping on edge	Increased chipping on edge	No Change	No Change
L-3	Minute fish-scale 6/cm^2	No Change	No Change	Minute fish-scale 10/cm^2	No Change
T	Sandy & minute fishscale 10/cm^2	No Change	No Change	No Change	No Change

TABLE XVII (Continued)

WATER JET QUENCH OF 4- X 8- INCH PLATES
COATED WITH -S- ENAMEL

Type of Steel	800°F Quench Cycles				
	1	2	3	4	5
N-1	Sandy	No Change	No Change	No Change	No Change
N-2	Sandy	No Change	No Change	No Change	No Change
W-1	Sandy	No Change	No Change	No Change	No Change
W-2	Sandy	No Change	No Change	No Change	No Change
W-3	Sandy & Minute Fishscale $16/cm^2$	No Change	No Change	No Change	No Change

Note: No changes were noted on any of the samples during the five quenches from 900°F

TABLE XVIII

WATER JET QUENCH OF 4- X 8- INCH PLATES
COATED COMMERCIALLY

Type of Steel	BEFORE QUENCH	Average Coating Thickness
H	No Defect	5.5
J-1	1/16" fishscale (exposing bare metal) disqualified	8.0
J-2	No Defect	6.5
L-1	1/16" fishscale (no exposed metal)	7.8
L-2	No Defect	5.8
L-3	No Defect	7.3
T	No Defect	7.8
N-1	No Defect	5.3
N-2	1/4" chips on edge	7.5
W-1	No Defect	6.5
W-2	1/4" fishscale (exposing bare metal) disqualified	6.5
W-3	No Defect	6.0

Type of Steel	650°F Quench Cycle				
	1	2	3	4	5
H	No Change	No Change	No Change	No Change	No Change
J-2	(14)1/16" chips (no exposed metal)	No Change	No Change	No Change	(2)1/8" edge chips
L-1	(4)1/8" chips (no exposed metal)	(3) 3/16" chips on edge	No Change	No Change	No Change
L-2	No Change	No Change	(1) 1/4" edge chip	No Change	(1)1/4" edge chip
L-3	No Change	3/16" chip on edge (1)	No Change	No Change	No Change
T	Minute fish-scale 3/cm^2	3/16" chip on edge (1)	No Change	No Change	No Change

TABLE XVIII (Continued)

WATER JET QUENCH OF 4- X 8- INCH PLATES
COATED COMMERCIALLY

Type of Steel	650°F Quench Cycle 1	2	3	4	5
N-1	No Change	No Change	(1)1/8" edge chip	No Change	No Change
N-2	No Change	No Change	No Change	No Change	No Change
W-1	No Change	(1)3/16" edge chip	No Change	No Change	(1)1/4" edge chip
W-3	No Change	(3)1/4" edge chips	No Change	No Change	No Change

Type of Steel	800°F Quench Cycle 1	2	3	4	5
H	(2)1/4" corner chips	(1)3/16" edge chip	(1)3/16" edge chip	(3)1/8" edge chips	No Change
J-2	No Change	No Change	(1)1/8" edge chip	(3) 1/8" edge chips	(1)1/16" chip
L-1	No Change	No Change	(9)1/8" edge chips - large fishscale (disqualified)		
L-2	(1)1/4" edge chip	No Change	(2)1/8" edge chips	(2)1/8" edge chips	No Change
L-3	No Change	No Change	No Change	No Change	No Change
T	(1)3/16" edge chip	(2)1/8" edge chips	(7)3/16" edge chips	(7)1/8" edge chips exposed metal (disqualified)	
N-1	No Change	No Change	No Change	(1)1/8" corner chip	(1)1/6" chip

TABLE XVIII (Continued)

WATER JET QUENCH OF 4- X 8- INCH PLATES
COATED COMMERCIALLY

Type of Steel	800°F Quench Cycle				
	1	2	3	4	5
N-2	No Change	No Change	(1)1/8" edge chip	(3)1/16" edge chips	1/16" chips exposing bare metal
W-1	(1)3/16" edge chip	(1)1/8" corner chip	(1)1/8" corner chip	No Change	(1)1/16" chip
W-3	No Change	No Change	No Change	(1)1/8" edge chip	(6)1/16" edge chips

Type of Steel	900°F Quench Cycles				
H	No Change	(1)1/8" corner chip	No Change	No Change	(4)1/8" edge chips exposing bare metal Disqualified
J-2	No Change	No Change	No Change	No Change	(3)1/16" edge chips
L-2	No Change	No Change	No Change	(4)1/8" edge chips	(8)1/16" edge chips
L-3	(1)1/16" corner chip	(1) 1/16" edge chip	(2)1/8" edge chips	No Change	(2)1/8" edge chips
N-1	(3)1/8" edge chips	No Change	No Change	(4)1/8" edge chips	(5)1/16" edge chips
W-1	(2)1/8" corner chips	No Change	No Change	No Change	(2)1/16" edge chips
W-3	(2) 3/16" edge chips	(4)1/8" edge chips	No Change	No Change	(2)1/16" corner chips

TABLE XIX

IMMERSION QUENCH OF T-JOINTS COATED COMMERCIALLY

T-Joint	Before Quench
H	Tearing
J-1	3/8" fishscale exposing bare metal completely covering 3/16 inch plate (DISQUALIFIED)
J-2	Fishscale (No exposed metal)
L-1	Chipping on edges and on 5/8" metal
L-2	Fishscale on Welded Area
L-3	Large chips on weld
T	Chips on edges
N-2	1/16" fishscale (all in line across) bottomside of 3/16 inch plate

T-Joint	650°F Quench Cycles				
	1	2	3	4	5
H	No Change	Large chips on edge 3/8"	No Change	No Change	No Change
J-2	Chips on 5/8" metal	Increased chipping on 5/8" metal	No Change	Minute fishscale	No Change
L-1	No Change	No Change	Chip on 5/8" would be disqualification	Fishscale on 3/16" bottom	No Change
L-2	No Change	No Change	Large chip on 3/16 metal (DISQUALIFIED)	------	-----
L-3	No Change	Chipping on 5/8" metal	1/8" chip on bottom of 3/16"	Chips on 5/8" metal	No Change
T	No Change	No Change	Chips on 5/8" metal	Chips on 5/8" metal	No Change
N-2	No Change	Increased fishscale	3 - 1/16" fishscales on bottom	No Change	No Change

TABLE XIX (Continued)

IMMERSION QUENCH OF T-JOINTS COATED COMMERCIALLY

Type of Steel	800°F Quench Cycles 1	2	3	4	5
H	No Change	More chipping on edges of 3/16	Increased chipping	No Change	No Change
J-2	No Change	Chipping on edges	Increased chipping	Increased chipping	No Change
L-1	Chip on edge of 3/16 metal	chipping on edges	Increased chipping	Increased chipping	No Change
L-3	Large fish-scale (Disqualified)	----------	----------	----------	----------
T	Edge chip on 3/16 metal	Increased chipping	Increased chipping	Increased chipping	No Change
N-2	No Change	Increased chipping	Increased chipping	No Change	No Change

Type of Steel	900°F Quench Cycles 1	2	3	4	5
H	No Change	Increased chipping	Increased chipping	Increased chipping	No Change
J-2	No Change	Increased chipping	No Change	No Change	No Change
L-1	No Change	No Change	Increased chipping	Increased chipping	No Change
T	No Change	Increased chipping	Increased chipping	Increased chipping	No Change
N-2	No Change	No Change	Increased chipping	No Change	No Change

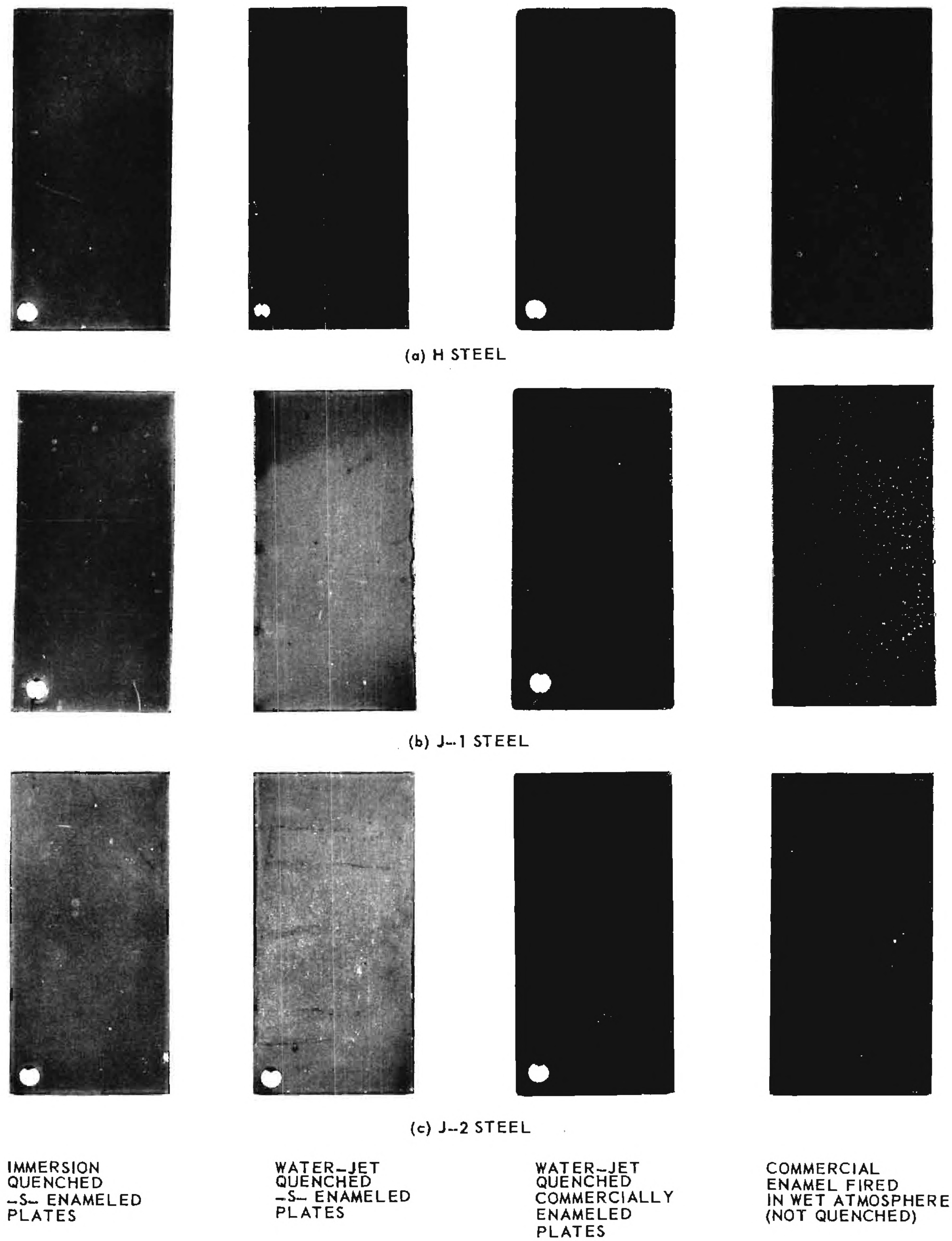


Figure 26. Enameled 4- by 8-Inch Specimens.

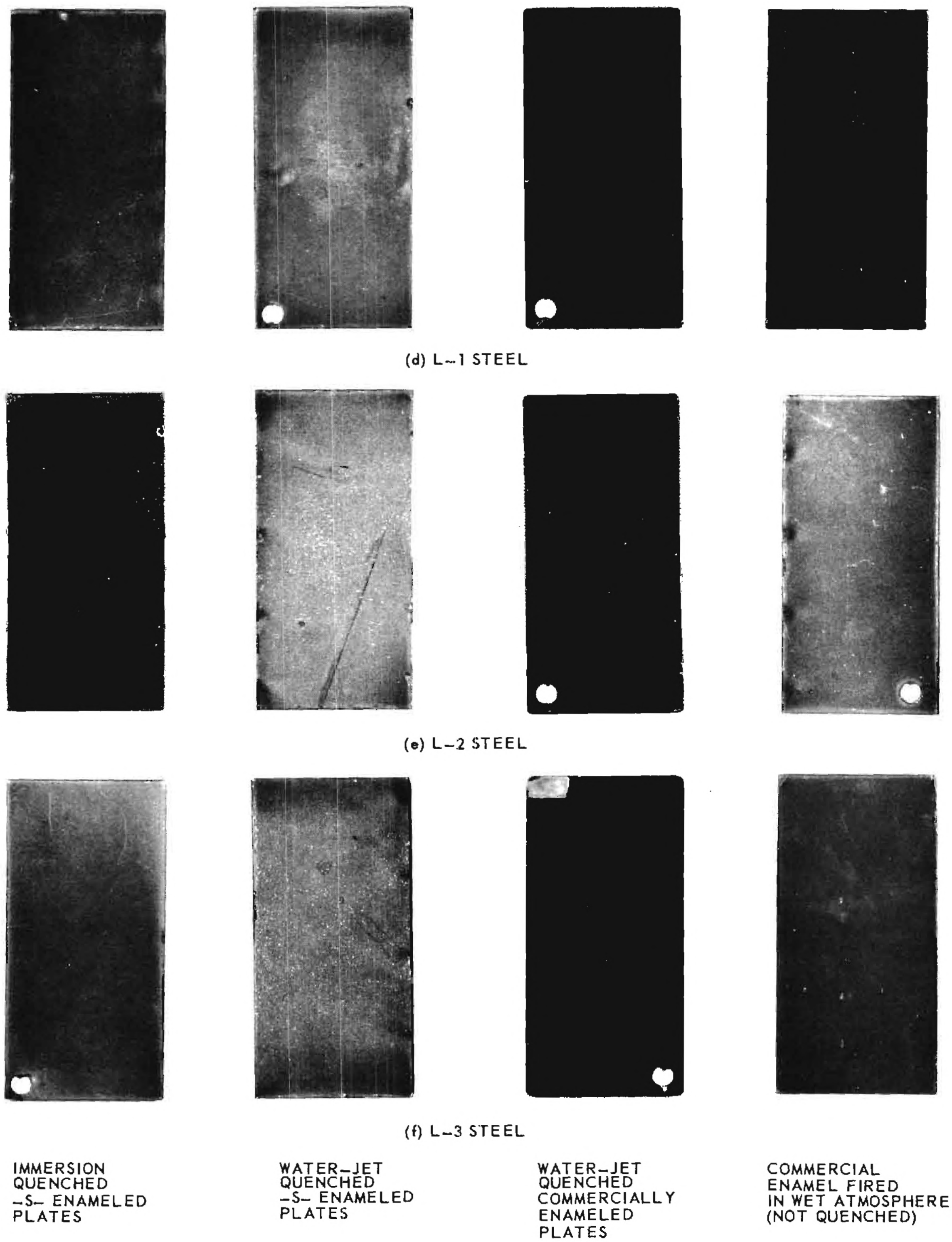


Figure 26 (Continued). Enameled 4- 8-Inch Specimens.

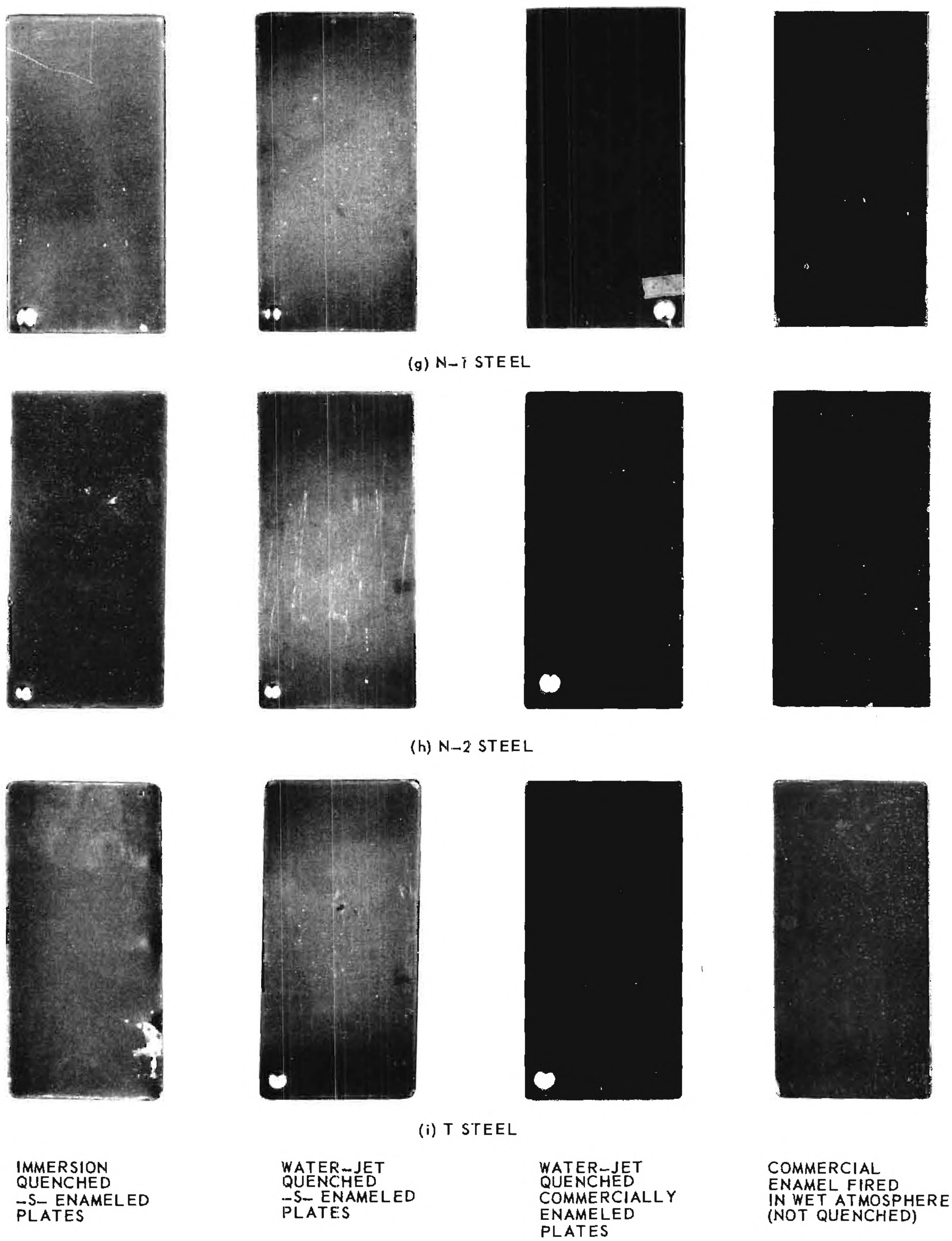
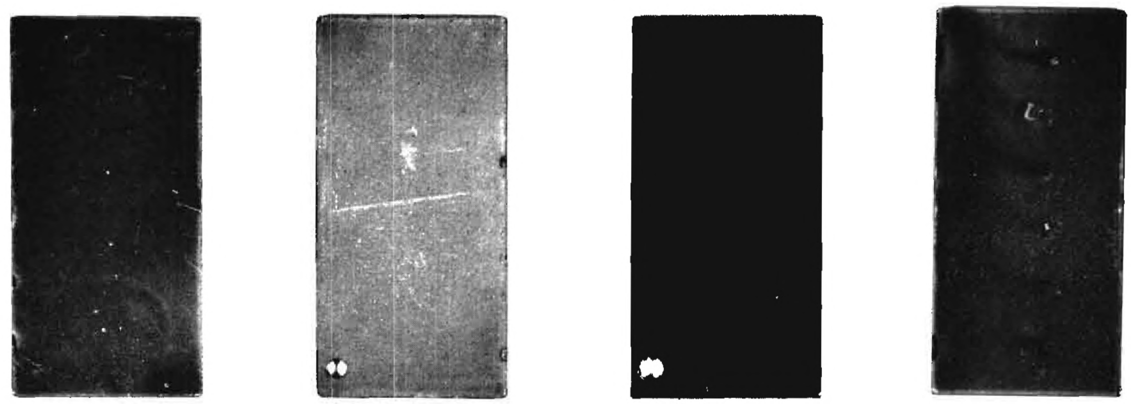
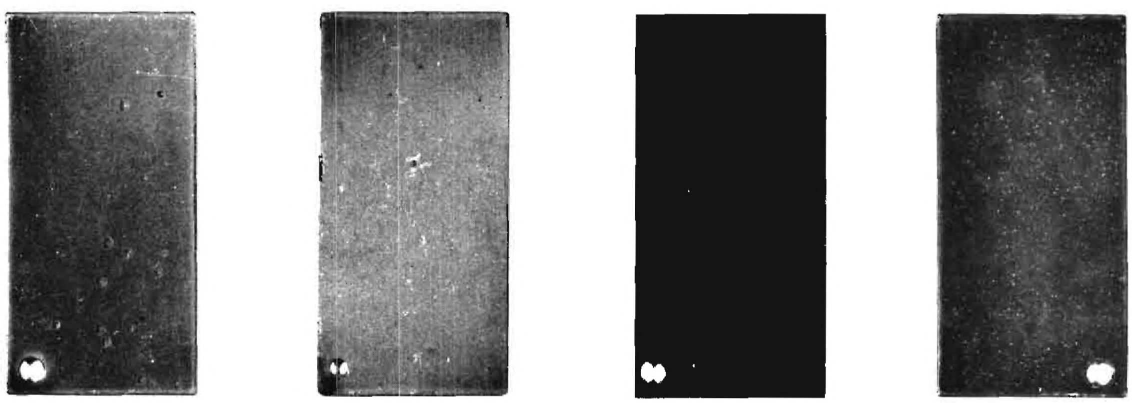


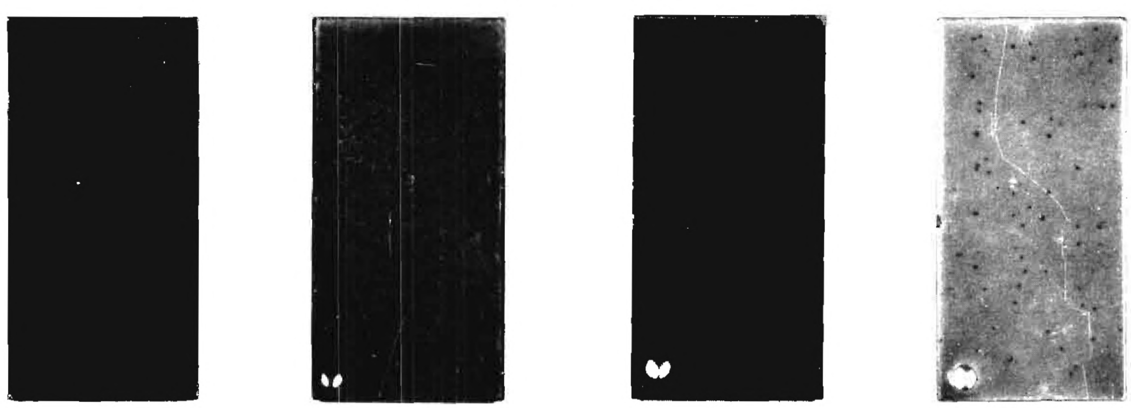
Figure 26 (Continued). Enameled 4- 8-Inch Specimens.



(j) W-1 STEEL



(k) W-2 STEEL



(l) W-3 STEEL

IMMERSION QUENCHED -S- ENAMELED PLATES

WATER-JET QUENCHED -S- ENAMELED PLATES

WATER-JET QUENCHED COMMERCIALLY ENAMELED PLATES

COMMERCIAL ENAMEL FIRED IN WET ATMOSPHERE (NOT QUENCHED)

Figure 26 (Continued). Enameled 4- 8-Inch Specimens.

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Companies who Furnished Steel Plate at no Cost

Jones and Laughlin Steel Corporation
No. 3 Gateway Center
Pittsburgh 30, Pennsylvania

Attention: Mr. Ralph Miller, Assistant Manager
Sheet Mill Products

Lukens Steel Company
Coatesville, Pennsylvania

Attention: Mr. Louis K. Keay, Manager
Technical Service

Alan Wood Steel Company
Conshohochken, Pennsylvania

Attention: Mr. Robert H. Lubker, Director
Research and Development

Bethlehem Steel Company
Bethlehem, Pennsylvania

Attention: Mr. P. D. Ffield
Assistant Manager of Research

The Youngstown Sheet and Tube Company
Youngstown 1, Ohio

Attention: L. E. Arnold, Manager
Flat Rolled Sales

United States Steel Corporation
Applied Research Laboratory
Monroeville, Pennsylvania

Attention: R. W. Vanderbeck, Chief Res. Eng.
Structural and Plates

*Great Lakes Steel Corporation
Ecourse
Detroit, Michigan

Attention: Mr. D. A. Schaitberger
Product Development Division

* Steel plates arrived too late for inclusion in study because of steel strike, however, were received at no cost to contract or government.